THE ELECTRODEPOSITION OF MOLYBDENUM ALLOYS[1]

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ABSTRACT

A new aqueous citrate plating bath for the electrodeposition of alloys of molybdenum with cobalt, iron, and nickel is described. This type of plating solution contains the sulfate of the codepositing metal citric acid, and sodium molybdate. Ammonium hydroxide is used for adjusting the pH of the solution. A bath temperature of about 25 C is preferred. Experimental results, obtained by using the Hull cell for qualitative information and regular plating procedures for quantitative data, show the effect of bath pH, concentration of sodium molybdate, and cathode current density on the performance of the plating baths. The highest percentage of molybdenum (about 50% and more) is obtained with iron as the codepositing metal, and the lowest is with nickel.

INTRODUCTION

The electrodeposition of molybdenum from aqueous solutions has been reported a number of times, but there is some doubt as to whether or not metallic molybdenum has been electrodeposited from aqueous solutions in appreciable amounts. In 1896, Férée (1) studied the electrolytic reduction of Mo(VI) compounds to the metal at a mercury cathode. Myers (2) and Merrill and Russell (3) also used mercury cathodes in their work on the reduction of aqueous molybdate solutions. Chilesotti (4) used various types of solutions and cathode materials with negative results. A patent, issued to Fink and Eldridge (5) in 1927, claims the electrodeposition of metallic molybdenum from a saturated solution of molybdic acid. In 1932, Yntema (6) reported the electrodeposition of molybdenum from a citrate solution. In 1934, Krause (7) reported the deposition of black deposits of molybdenum from solutions of ammonium molybdate, and Pokorny and Schneider (8) claimed in a patent that thin electrodeposits of molybdenum could be obtained from strongly alkaline solutions saturated with molybdenum(VI) oxide. In 1936, Price and Brown (9) reported the electrodeposition of molybdenum from solutions of molybdic acid in sulfuric acid. Two Russian patents (10) also make some claims for the successful electrodeposition of molybdenum from several types of aqueous solutions.

The successful electrodeposition of tungsten alloys from various aqueous solutions (11, 12) and the fact that molybdenum and tungsten are quite similar in chemical behavior suggests that the electrodeposition of molybdenum alloys should be possible, and reports in the literature indicate some degree of success. In 1939, Hoffman and Hull (13) reported the deposition of black molybdenum finishes which contain nickel and molybdenum. In 1946, Blum (14) mentioned that the electrodeposition of molyb-

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denum alloys had been studied at the Bureau of Standards as a wartime research. Recently, Yntema (15) was granted a patent for the electrodeposition of cobalt-molybdenum and iron-molybdenum alloys from strongly alkaline solutions containing dextrose as the complexing agent.

The purpose of this article is to report the results of a study of the electrodeposition of alloys of molybdenum with nickel, with cobalt, and with iron from aqueous citrate solutions. The present work was limited to citrate solutions and these three alloying metals, because it seemed desirable to compare the results with similar work on tungsten alloy deposition (16, 17, 18) previously reported from this laboratory. The development of a practical aqueous plating bath for the electrodeposition of molybdenum alloys was not the primary objective; rather, the main goal was the acquisition of new information about the electrolytic reduction of aqueous molybdate solutions.

EXPERIMENTAL METHODS

Bath preparation.—Anhydrous sodium molybdate, Na_2MoO_4, was the molybdenum compound used in preparation of the plating baths. Other compounds were reagent grade, and the baths were usually prepared directly from the crystalline materials. Bath pH was adjusted as required by the addition of ammonium hydroxide. In all cases the pH was determined by a glass electrode at the operating temperature of the bath.

Hull cell.—This cell (267 ml size) was used in making preliminary investigations with the various baths. The Hull cell (19) is well suited for this purpose because it gives qualitative information about the effect of bath composition and operating conditions over a fairly wide range of current densities. In all cases it was used with a copper cathode, 2½ in. x 4 in. (6.4 cm x 10.2 cm), and a platinum anode, 2½ in. x 2½ in. (6.4 cm x 6.4 cm), with a total current of three amperes.

Electrolysis.—The electrolysis apparatus was similar to that previously described (16) with an arrangement for operating several electrolysis cells simultaneously. For most of the work, about 200 ml of plating solution was used in each cell. Direct current was supplied by a selenium rectifier unit equipped with a variac, an ammeter, and a voltmeter. Bath temperatures were maintained by means of a thermostat. Platinum anodes and cathodes, 3 x 3 cm, were used in all regular plating runs. Cathode current efficiencies (C.C.E.) were calculated from the analysis of the deposit and the weight of copper deposited in a copper coulometer which was connected in series for each electrolysis.

Analysis of deposits.—The cathode deposit to be analyzed was dissolved by boiling with 4N nitric acid. The platinum cathode was then removed from the solution and washed. The codepositing metal—nickel, cobalt or iron—was separated from molybdenum by precipitation with sodium hydroxide. Molybdenum was determined gravimetrically by precipitation as lead molybdate. Nickel and cobalt were determined electrolytically from a strongly ammoniacal solution. Iron was determined volumetrically by titration with potassium dichromate using the Zimmermann-Reinhardt method.

EXPERIMENTAL RESULTS

Three different citrate plating baths were used in the experimental work: (1) the cobalt-molybdenum bath, (2) the nickel-molybdenum bath

and (3) the iron-molybdenum bath. The mole ratio of citric acid and the codepositing metal in these baths was kept constant—approximately 1.5 to 1. Bath variables were the amount of sodium molybdate, pH, cathode current density (C.C.D.), and temperature. Qualitative information about a given bath was first obtained by means of the Hull cell; then, quantitative information about cathode current efficiency (C.C.E.) and the composition of the cathode alloy deposit was obtained by regular plating procedures.

THE COBALT-MOLYBDENUM BATH

This bath contained 60 g/l of $CoSO_4 \cdot 7H_2O$, 66 g/l of citric acid, and variable amounts of sodium molybdate. The bath pH was adjusted as required with ammonium hydroxide.

Bath temperature.—Hull cell observations and quantitative results showed that a bath temperature of 25 C was preferable to a bath temperature of 70 C. Lower cathode current densities could be employed at the lower temperature, and, also, the bath at 25 C was much less sensitive to changes in the concentration of sodium molybdate than the higher temperature bath. Thus, a temperature of about 25 C was used for all additional work with this bath.

Bath pH.—The effect of pH was determined using a bath containing 4 g/l of sodium molybdate and a pH range of 3 to 9. Hull cell results showed that the cathode current density range of bright plating and the appearance of the deposit were markedly influenced by the pH of the plating bath. These results are shown schematically in Fig. 1 where each area represents a Hull cell cathode.

The effect of pH was then determined quantitatively using regular plating procedures. The cathode current efficiency and the percentage of molybdenum in the deposit were determined at a number of different pH values and at a high, a medium, and a low cathode current density. The results, given in Fig. 2, show that the molybdenum content of the cathode deposit increases rather regularly with increasing bath pH (less acid), while the cathode current efficiency increases to a maximum and then decreases sharply as the bath is made more basic.

Concentration of sodium molybdate and cathode current density.—Since pH studies indicated that acid baths were the most satisfactory, pH values of 3 and 4 were used while determining the effect of the sodium molybdate concentration on the performance of the bath. Hull cell cathodes were uniformly bright at sodium molybdate concentrations as high as 40 g/l. Quantitative results, using pH 3 and several cathode current densities, showing the effect of sodium molybdate concentration on the cathode current efficiency and the composition of the alloy deposit are given in Fig. 3. The cathode current efficiency and percentage of molybdenum in the deposit increase as the amount of sodium molybdate in the bath is increased and the cathode current efficiency decreases as the cathode current density is increased. Somewhat similar results were obtained using a bath pH of 4 although these results were not so reproducible as when the bath was operated at pH 3.

THE NICKEL-MOLYBDENUM BATH

This bath contained 60 g/l of $NiSO_4 \cdot 6H_2O$, 66 g/l of citric acid, and variable amounts of sodium molybdate. The bath pH was adjusted by the addition of ammonium hydroxide.

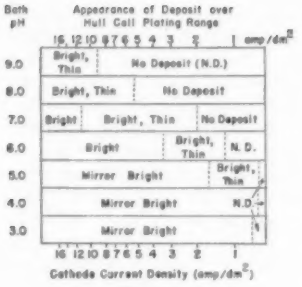
Bath pH
Appearance of Deposit over Hull Cell Plating Range
16 12 10 8 7 6 5 4 3 2 1 amp/dm²
9.0 Bright, Thin | No Deposit (N.D.)
8.0 Bright, Thin | No Deposit
7.0 Bright | Bright, Thin | No Deposit
6.0 Bright | Bright, Thin | N. D.
5.0 Mirror Bright | Bright, Thin
4.0 Mirror Bright | N.D.
3.0 Mirror Bright
16 12 10 8 7 6 5 4 3 2 1
Cathode Current Density (amp/dm²)

FIG. 1

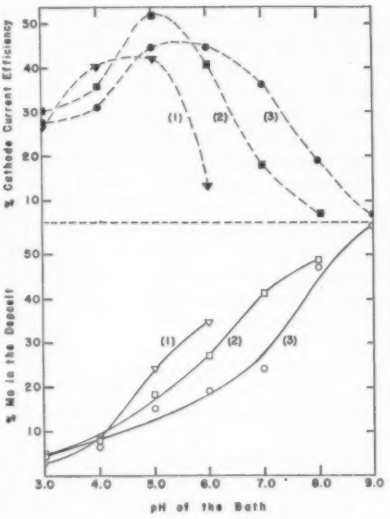

FIG. 2

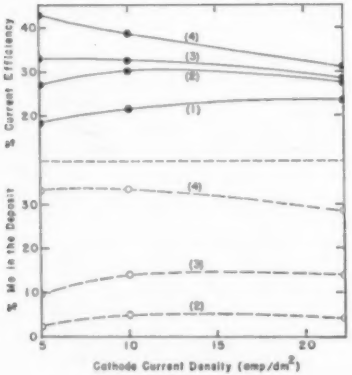

FIG. 3

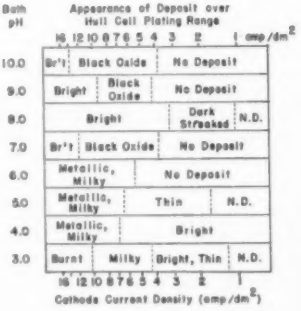
Bath pH
Appearance of Deposit over Hull Cell Plating Range
16 12 10 8 7 6 5 4 3 2 1 amp/dm²
10.0 Br't | Black Oxide | No Deposit
9.0 Bright | Black Oxide | No Deposit
8.0 Bright | Dark Streaked | N.D.
7.0 Br't | Black Oxide | No Deposit
6.0 Metallic, Milky | No Deposit
5.0 Metallic, Milky | Thin | N.D.
4.0 Metallic, Milky | Bright
3.0 Burnt | Milky | Bright, Thin | N.D.
16 12 10 8 7 6 5 4 3 2 1
Cathode Current Density (amp/dm²)

FIG. 4

FIG. 1. Appearance of Hull cell cathodes, showing the effect of pH on the cobalt-molybdenum bath (Na_2MoO_4, 4 g/1; temp 25 C; 3 amp for 3 min). *Note:* In this figure and subsequent similar figures, the height of the cathode relative to its length is decreased considerably in order to conserve space.

FIG. 2. The effect of pH on the cobalt-molybdenum bath at three current densities (Na_2MoO_4, 4 g/1; temp 25 C). Curve 1 = 5 amp/dm²; curve 2 = 10 amp/dm²; curve 3 = 22.2 amp/dm².

FIG. 3. The effect of sodium molybdate concentration and cathode current density on the cobalt-molybdenum bath (pH 3; temp 25 C). Curve 1 = no Na_2MoO_4; curve 2 = 4 g/1 Na_2MoO_4; curve 3 = 20 g/1 Na_2MoO_4; curve 4 = 40 g/1 Na_2MoO_4.

FIG. 4. Appearance of Hull cell cathodes, showing the effect of pH on the nickel-molybdenum bath (Na_2MoO_4, 4 g/1; temp 25 C; 3 amp for 3 min).

Bath temperature.—This bath, like the cobalt-molybdenum bath, was found to give better results of 25 C than at 70 C. Metallic deposits were obtained at lower current densities, and, in general, the character of the deposits was better at the lower bath temperature.

Bath pH.—The effect of pH was determined using a bath containing 4 g/l of sodium molybdate and pH values from 3 to 10. The use of the Hull cell showed that bath pH has a marked effect on the character of the plates obtained. These Hull cell results are shown in Fig. 4. Both pH 4 and pH 8 give bright plates at a fairly wide current density range, although fairly high current densities are required at pH 8.

A cathode current density of 22.2 amp/dm^2 was used in a quantitative study of the effect of bath pH on cathode current efficiency and percentage of molybdenum in the cathode deposit. The results of this work are given

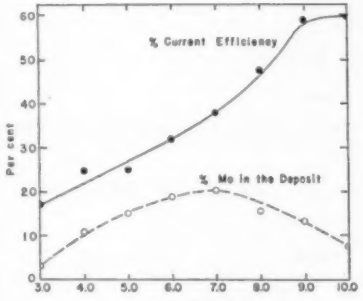

FIG. 5

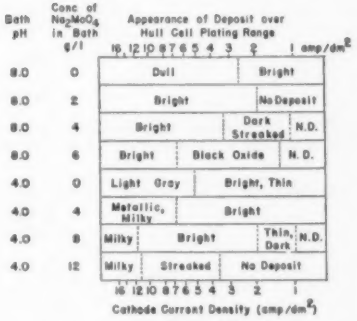
Bath pH
Conc of Na_2MoO_4 in Bath g/l
Appearance of Deposit over Hull Cell Plating Range
16 12 10 8 7 6 5 4 3 2 1 amp/dm²
8.0 0 Dull Bright
8.0 2 Bright No Deposit
8.0 4 Bright Dark Streaked N.D.
8.0 6 Bright Black Oxide N. D.
4.0 0 Light Gray Bright, Thin
4.0 4 Metallic, Milky Bright
4.0 8 Milky Bright Thin, Dark N.D.
4.0 12 Milky Streaked No Deposit
16 12 10 8 7 6 5 4 3 2 1
Cathode Current Density (amp/dm²)

FIG. 6

FIG. 5. The effect of pH on the nickel-molybdenum bath (Na_2MoO_4, 4 g/1; temp 25 C; C.C.D. 22.2 amp/dm^2).

FIG. 6. Appearance of Hull cell cathodes, showing the effect of sodium molybdate concentration on the nickel-molybdenum bath at pH 4 and pH 8 (temp 25 C; 3 amp for 3 min).

in Fig. 5. It can be seen that this bath is quite different from the cobalt-molybdenum bath, with the cathode current efficiency increasing regularly and the percentage of molybdenum rising to a maximum and then decreasing as the bath pH is increased. At a cathode current density of 10 amp/dm^2 the results were similar, except that nonmetallic cathode deposits were obtained at a bath pH of 7.

Concentration of sodium molybdate.—Two bath pH values, 4 and 8, were used in the study of the effect of the concentration of sodium molybdate. Hull cell results, given in Fig. 6, show that the concentration of sodium molybdate is an important factor. Quantitative results at a pH of 8 and a high cathode current density, 22.2 amp/dm^2, are given in Fig. 7. The percentage of molybdenum in the deposit increases regularly and cathode current efficiency increases to a maximum and then decreases as the concentration of sodium molybdate in the bath is increased.

Cathode current density.—A rather complete quantitative study was made on the effect of cathode current density on the nickel-molybdenum bath. A bath pH of 4 was used, the concentration of sodium molybdate

was varied from 0 to 12 g/l, and cathode current density was varied from 1 to 22.2 amp/dm². The results, given in Table I, show that cathode current efficiency increases sharply and then drops off as the cathode current density is increased, while the percentage of molybdenum in the deposits decreases regularly with increasing cathode current density.

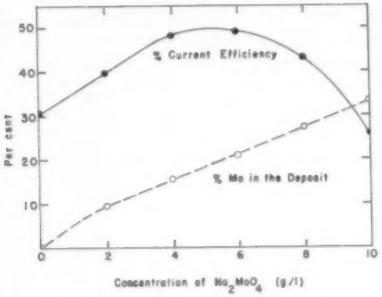

FIG. 7. The effect of sodium molybdate concentration on the nickel-molybdenum bath (temp 25 C; pH 8; C.C.D. 22.2 amp/dm²).

TABLE I. *The effect of cathode current density on the nickel-molybdenum bath* (pH 4.0, temp 25 C)

Conc of Na_2MoO_4	C.C.D. amp/dm²	Time min	Wt of deposit	Analysis		% C.C.E.	Character of deposit
				% Mo	% Ni		
(g/l)			(g)				
0	5.0	10	0.0387	—	100.0	22.9	dull
0	10.0	5	0.0311	—	100.0	17.1	dull
0	22.2	3	0.0389	—	100.0	16.1	gray
4	1.0	20	0.0040	23(?)	85(?)	7.1	tarnished
4	2.0	20	0.0398	19.7	79.7	35.0	bright
4	5.0	10	0.0469	16.9	83.2	31.9	bright
4	10.0	5	0.0390	13.0	87.7	24.2	bright
4	15.0	3	0.0362	11.6	86.4	25.5	dull
4	22.2	3	0.0521	10.8	88.2	24.8	dull
8	2.0	20	0.0121	27.3	72.7	9.3	stained
8	5.0	10	0.0412	23.8	75.1	29.8	bright
8	10.0	5	0.0443	18.5	80.4	27.0	milky
8	15.0	3	0.0336	14.2	84.8	23.2	milky
8	22.2	3	0.0438	10.3	88.7	20.1	milky
12	10.0	10	0.0650	27.4	71.7	22.5	slightly darkened
12	22.2	3	0.0440	17.2	81.3	20.8	bright

THE IRON-MOLYBDENUM BATH

This bath contained 60 g/l of $FeSO_4 \cdot 7H_2O$, 66 g/l citric acid, and variable amounts of sodium molybdate. The pH was adjusted by the addition of ammonium hydroxide. In preparing this bath, it was found best to use sodium molybdate solution rather than the solid material. It was necessary, in order to get consistent results, to use iron-molybdenum baths immediately after preparation.

Bath temperature.—No detailed study of temperature was made. However, the few plates obtained at 70 C were dark and stained, and contained smaller percentages of molybdenum.

Bath pH.—The effect of pH was determined with a bath containing 4 g/l of sodium molybdate and having pH values from 3 to 8. Hull cell results, presented in Fig. 8, show that pH has a marked effect on the bright plating range. It appears that a pH of 6 is the best.

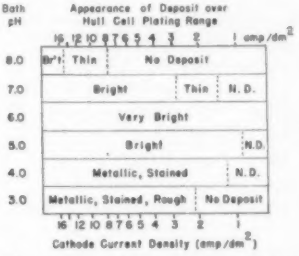

FIG. 8. Appearance of Hull cell cathodes, showing the effect of pH on the iron-molybdenum bath (Na_2MoO_4, 4 g/1; temp 25 C; 3 amp for 3 min).

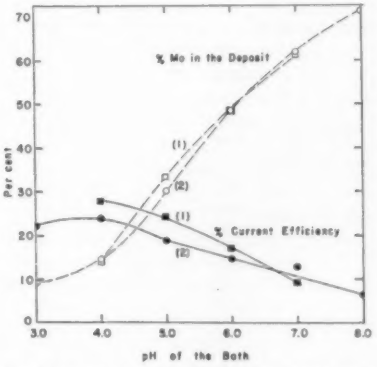

FIG. 9. The effect of pH on the iron-molybdenum bath at two current densities (Na_2MoO_4, 4 g/1; temp 25 C). Curve 1 = 10 amp/dm²; curve 2 = 22.2 amp/dm².

Two cathode current densities, 10 and 22.2 amp/dm², were used in a quantitative study of the effect of pH on cathode current efficiency and on the percentage of molybdenum in the cathode deposit. The results are given in Fig. 9 and show that this bath behaves in about the same manner as the cobalt-molybdenum bath with, however, much lower cathode current efficiencies.

Concentration of sodium molybdate and cathode current density.—A pH of 6 was used for most of the work determining the effect of the concentration of sodium molybdate and cathode current density. Hull cell results, given in Fig. 10, show that the molybdate concentration is quite critical

at pH 6 although not so critical at pH 4. Apparently, a concentration of 4 g/l of sodium molybdate, at pH 6, gives the best plate.

A brief quantitative study was made on the effect of these variables on cathode current efficiency and percentage of molybdenum in the deposit. A bath pH of 6, several concentrations of sodium molybdate, and a number of different cathode current densities were used. The results, given in Table II, show that cathode current density, in the range studied, has only

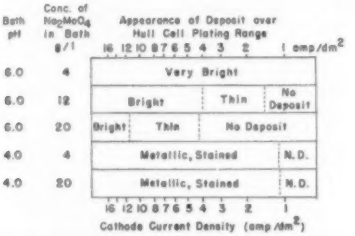
Bath pH
Conc. of Na_2MoO_4 in Bath g/l
Appearance of Deposit over Hull Cell Plating Range
16 12 10 9 8 7 6 5 4 3 2 1 amp/dm²
6.0 4 Very Bright
6.0 12 Bright Thin No Deposit
6.0 20 Bright Thin No Deposit
4.0 4 Metallic, Stained N.D.
4.0 20 Metallic, Stained N.D.
16 12 10 9 8 7 6 5 4 3 2 1
Cathode Current Density (amp/dm²)

FIG. 10. Appearance of Hull cell cathodes, showing the effect of sodium molybdate concentration on the iron-molybdenum bath at pH 4 and pH 6 (temp 25 C; 3 amp for 3 min).

TABLE II. *The effect of cathode current density and Na_2MoO_4 concentration on the iron-molybdenum bath*

(pH 6.0, temp 25 C)

Conc of Na_2MoO_4	C.C.D. amp/dm²	Time min	Wt of deposit	Analysis		% C.C.E.	Character of deposit
				% Mo	% Fe		
(g/l)			(g)				
4	5.0	20	0.0429	53.0	42.9	18.4	bright
4	10.0	10	0.0431	48.6	49.5	17.1	bright
4	15.0	7	0.0415	51.1	44.4	15.9	bright
4	22.2	4	0.0379	48.6	48.3	14.7	bright
12	10.0	15	0.0244	56.6	38.3	6.7	stained
12	22.2	5	0.0342	58.5	36.5	12.9	bright
20	22.2	5	0.0267	58.9	34.3	9.7	stained

a slight effect on composition of the cathode deposit and cathode current efficiency.

DISCUSSION

It is interesting to compare these three molybdenum alloy plating baths. Under similar conditions, the highest percentage of molybdenum was obtained with iron as the codepositing metal and the lowest with nickel. In general, highest current efficiencies were obtained with the nickel-molybdenum bath and the lowest with the iron-molybdenum bath, although at pH 4, the current efficiencies were about the same, and at pH 5, the cobalt-molybdenum bath showed the highest efficiency. In a number of respects the cobalt-molybdenum and iron-molybdenum baths are quite similar. They showed the same general effect of pH on cathode current

efficiency, and much the same small effect of sodium molybdate concentration at pH 4. Also, in basic solutions, these baths gave metal deposits only at high current densities and with low current efficiencies. The baths are somewhat different in that the optimum pH for the cobalt-molybdenum bath was 4, whereas, for the iron-molybdenum bath it was 6. The nickel-molybdenum bath is quite different from the other two baths in that current efficiency increased with increasing pH, and satisfactory deposits were obtained from alkaline solutions.

There are, no doubt, complex ions present in this citrate type of molybdenum alloy plating bath. The codepositing metals are perhaps complexed with the citrate ion, but the identity of the molybdate ion in the bath is questionable. Normal molybdates, $MoO_4^{=}$, are said to be stable only in basic solutions except at very low concentrations. As the acidity of a molybdate solution is increased, the complexity of the anion increases; for example, at a pH of 4, the ionic species is said to be $(Mo_6O_{21})^{-6}$, a hexamolybdate. Thus, it is to be expected that the use of higher concentrations of molybdate would be possible in the bath at the lower pH values because the number of ions decreases. Also, the percentage of molybdenum in the alloy deposit should decrease with increasing complexity of the molybdate ions present near the cathode surface. This was found to be so, especially with the cobalt-molybdenum and iron-molybdenum baths, and, to a lesser extent, with the nickel-molybdenum bath at pH values of 6 and below.

The present experimental work is recognized as being too limited in scope to make possible an explanation for the codeposition of molybdenum with cobalt, nickel, and iron. Possibly, the recently proposed "catalytic reduction" theory (11), explaining the electrodeposition of tungsten alloys, can be applied to molybdate solutions. It seems quite probable that the cathode processes involved in the electrolytic reduction of tungstates and molybdates in the presence of nickel, iron, and cobalt cations are the same or, at least, are very similar. In support of this suggestion, this laboratory has recently found that ternary alloys, containing tungsten, molybdenum, and a codepositing metal, can be electrodeposited from a citrate type of plating bath. Certainly, more theoretical studies must be made before a reasonable explanation can be presented.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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A HIGH-EFFICIENCY ANODE FOR ALKALINE TIN-PLATING

The Effect of Alloying Constituents on the Anodic Behavior of Tin in Alkaline Stannate Solutions[1]

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ABSTRACT

By incorporating up to about 1 per cent of aluminum in the tin anodes used in alkaline tin plating, the current densities obtainable can be markedly increased. The effect of twenty-six elements upon the anode behavior of tin in alkaline solutions has been studied. Many have little effect in the quantities tested, i.e., up to about 1 per cent; some, such as nickel, silver, cadmium, and indium have a strong passivating action. Among the several which tend to increase anode efficiency, aluminum appears most promising from a practical standpoint, since it alloys smoothly and easily with tin, is nonpoisonous, cheap, produces no observable deleterious effect on the bath, and forms alloys which are stable and of good mechanical properties.

This investigation placed principal emphasis upon the potassium stannate bath, but enough work was done with the sodium stannate solution to show that the benefits of the aluminum alloy are common to both.

INTRODUCTION

It has been shown previously (2) that the potassium stannate bath possesses several advantages over the sodium stannate solution for tin plating; it permits the use of much higher cathode current densities, possesses higher conductivity, and evinces less tendency to hydrolysis or sludge formation. In general, however, anode efficiencies in the potash bath showed no improvement over those in the soda solution.

Thus the practical utilization of the high cathode current densities obtainable with the potash bath was subject to certain limitations; either the anode current density had to be kept low, or solutions relatively high in free KOH had to be used. The first alternative requires that the ratio of anode area to cathode area be greater than 1, and the higher the better; this condition may not always be fulfilled because of the geometry of plating installations. Because the tin or stannate content must likewise be raised to compensate for the deleterious effect on the cathode efficiency of increased free alkali, the second alternative leads to rather concentrated solutions.

Improvements in anodic efficiency ought, therefore, to widen substantially the field of usefulness of the potassium stannate solution. Since tests had already shown (3) that most common anions had little or no effect on the anode efficiency, such improvement was sought by means of changes in the composition of the anode itself, in the form of minor amounts of

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alloying elements. In addition to the positive results (the marked improvement obtainable with aluminum), it is believed that the negative results will also be of interest in so far as they indicate those metallic impurities which may give rise to trouble when present in tin anodes.

Literature

The influence of minor amounts of silver, iron, nickel, and copper upon the mechanical properties of tin has been reported by Hanson, Sandford, and Stevens (4), and that of aluminum, manganese, and bismuth by Hanson and Sandford (5). N. O. Taylor (6) reported some miscellaneous observations on the physical properties and corrosion of tin containing aluminum and zinc, although in rather larger amounts than concern us here. In a review article, Mantell (7) reported upon the corrosion of tin alloys; and Derge and Markus (8) have studied the effects of minor quantities of copper, zinc, nickel, iron, lead, silver, indium, magnesium, cadmium, antimony, bismuth, and calcium upon the corrosion of tin in carbonate solutions.

TABLE I. *Periodic arrangement of elements tested*

Series	Group											
	I		II		III		IV	V	VI	VII	VIII	
	a	b	a	b	a	b	b	b	a	a		
1												
2	Li											
3	Na		Mg			Al		P				
4			Ca						Cr	Mn	Fe, Co, Ni	
5		Cu		Zn		Ga	Ge	As				
6												
7		Ag		Cd		In	*Sn*	Sb				
8					La							
9		Au		Hg		Tl	Pb	Bi				

So far as appears in their publications, none of these workers tested tin alloys as anodes. Comparison between the results of the corrosion tests referred to and the work herein reported will show that there is little correlation, nor would any necessarily be expected. In a few cases, metals found by Derge and Markus (8) to render tin passive, i.e., corrosion resistant, in carbonate solutions, also had the effect of markedly reducing the anode efficiency in the present work, but such a correlation does not hold throughout.

In a recent patent (9), anodes of tin, alloyed with up to 10 per cent of an alkali metal, sodium or potassium, are claimed to show anode efficiencies substantially greater than that of pure tin. The present work was completed before that publication appeared. The effect of sodium and lithium as alloying elements is considered below.

EXPERIMENTAL

The metals chosen as additions to tin are shown in their periodic classification in Table I. At least one representative of every metallic group is

included in the test. The basis of choice of the metals was to some extent arbitrary, depending upon such factors as ready availability and possibility of preparing tin alloys without special equipment or involved techniques, but it is believed that few important elements have been omitted.

Anodes for test were cast in a graphite mold; they were 2 inches (5.1 cm) square and $\frac{1}{8}$ inch (3.2 mm) thick. Thickness was taken into account in determining the anode area. Two tin-plated steel cathodes were suspended on either side of the anode equidistant about $1\frac{1}{4}$ inches (3.2 cm) away.

All the exploratory tests were carried out in a constant-temperature oil bath which held the solutions at 90 ± 1 C. In these runs one liter of solution was contained in a 1500-ml beaker supported in the oil thermostat. Larger-scale confirmatory runs were made in 15-gallon (57 l) steel tanks.

In determining the anode efficiency, a high current was applied momentarily to film the anode, after which the current was lowered to the value

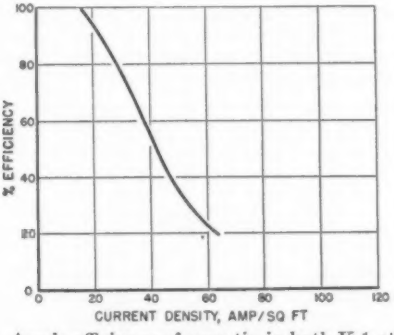

FIG. 1. Anode efficiency of pure tin in bath K-1 at 90 C

under test. Current was measured with an ammeter and time by means of an electric stopclock; product of current and time was so adjusted that the theoretical loss in weight of the anode was 100 mg or a simple multiple thereof, for simplicity in calculations.

Critical anode current densities were determined as in previous work (2).

The anode efficiency of pure tin was determined at the start of the series of experiments and also at frequent intervals during the course of the work, as a control. In most cases, the anodes were of American refined (M & T No. 1) tin, used as cast in the graphite mold; but a sample of cast Kahlbaum cp tin and a sample of rolled tin sheet, purchased from an outside source, were also tested and showed no difference in behavior.

Most of the work was done with a solution of the following composition:

Tin 40.5 g/l (0.34 mole/l)
Free KOH 11.5 g/l (0.20 mole/l)

and its sodium analogue

Tin 40.0 g/l (0.34 mole/l)
Free NaOH 7.9 g/l (0.20 mole/l)

These solutions will be designated No. K-1 and Na-1 respectively. Confirmatory experiments were carried out using solutions of other compositions, as will appear further on.

Fig. 1 and 2 show anode efficiencies of pure tin in solutions K-1 and Na-1 respectively.

RESULTS

We shall consider first the laboratory tests on each alloy, in solutions K-1 and Na-1. For a few alloys which appear especially interesting for any reason, anode efficiency curves are given. (The publication of such a curve for each alloy would unduly lengthen this paper.)

Lithium-tin.—The alloy contained 0.92 per cent Li. This alloy was very difficult to cast, and really smooth castings were never obtained; it was also quite brittle. The addition of lithium increased the anode efficiency in both solutions significantly, but the relative insolubility of

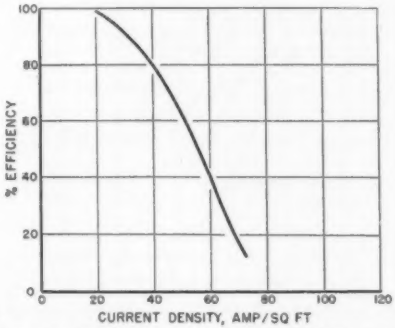

FIG. 2. Anode efficiency of pure tin in bath Na-1 at 90 C

lithium stannate as well as the poor mechanical properties of the alloy cancel its beneficial effects.

Sodium-tin.—A freshly prepared alloy containing 0.6 per cent Na was considerably better than pure tin in the potassium solution and somewhat better than tin in the sodium solution. However, on retesting this same alloy anode after a lapse of six months, some anomolous behavior was noted; it no longer possessed any advantage over pure tin. Further experimentation would have been necessary in order to determine the causes of such behavior, but in view of the superior results obtained with other alloying metals, notably aluminum, such additional work did not appear justified.

Copper-tin.—Copper (0.75%) had a passivating effect in both solutions.

Silver-tin.—One per cent silver significantly lowered the anode efficiency in both baths.

Gold-tin.—One per cent gold appeared to have little effect on the anode behavior.

Magnesium-tin.—Alloys of magnesium containing from 0.5 to 1.3 per

cent Mg were tested rather extensively. The reason for this additional attention was that early tests indicated high anode efficiencies for these alloys, but, on more thorough testing, an aging effect was noted. The beneficial effect of the magnesium decreased with the age of the alloys, until finally, after a few months, they had no advantage over pure tin. The alloys do not cast well and are somewhat brittle.

Calcium-tin.—One per cent Ca had little or no effect on the anode efficiency in either bath. The alloy is very brittle.

Zinc-tin.—One per cent Zn had little or no effect.

Cadmium-tin.—Cadmium was the worst "poison" found in this investigation. One per cent Cd markedly lowered the anode efficiencies in both baths, as shown in Fig. 3.

Mercury-tin.—Mercury (1%) appeared to be slightly beneficial, although probably within experimental error.

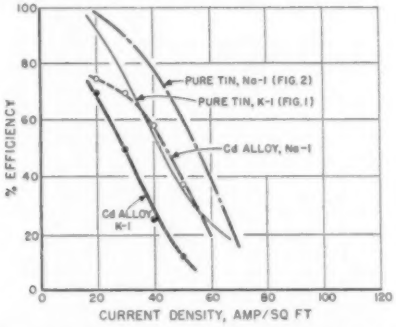

FIG. 3. Effect of cadmium (1%) on anode efficiency of tin at 90 C

Aluminum-tin.—Aluminum, in amounts above about 0.3 per cent, greatly increased the anode efficiency of tin. Because of its importance, detailed consideration of this alloy is reserved for a separate section.

Gallium-tin.—One per cent Ga raised the anode efficiency almost as much as did aluminum. It would be of definite interest if it were not for the scarcity and high price of this metal.

Indium-tin.—Indium (1%) is a definite poison in tin anodes, though not quite so bad as cadmium. This behavior contrasts with that of its close neighbor in the periodic table, gallium, just as in the case of the difference between zinc and cadmium.

Lanthanum-tin.—The 1% La-Sn alloy was tested in the potassium solution only, where it had little or no effect.

Thallium-tin.—One per cent Tl had a somewhat passivating effect.

Germanium-tin.—One per cent Ge has a definitely beneficial effect on the anode efficiency, but not enough to warrant a more thorough investigation in light of its price.

Lead-tin.—Lead (up to 1.5%) had somewhat different effects in the two solutions. In bath K-1, it had little influence in the low current-density, high-efficiency range, but tended to flatten the efficiency curve so

that it did not fall off so rapidly with increasing current density. In bath Na-1, it had a beneficial effect throughout the whole range. These facts are brought out in Fig. 4. However, the toxicity of lead and the fact that it would in all probability codeposit at the cathode precluded its serious consideration as an additive to tin.

Phosphorus-tin.—An alloy containing 0.66 per cent P was prepared using purchased phosphor-tin as a master alloy. The preliminary laboratory

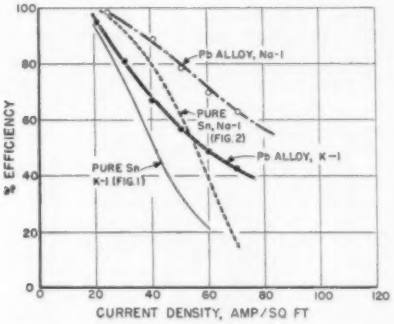

FIG. 4. Effect of lead (1%) on anode efficiency of tin at 90 C

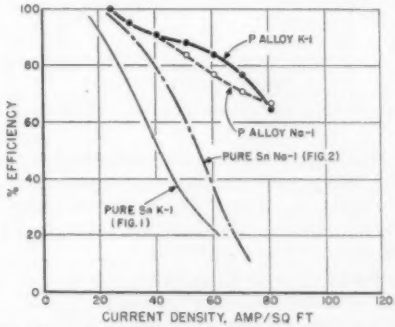

FIG. 5. Effect of phosphorus on anode efficiency of tin at 90 C

tests with this alloy as anode were very promising, since it was indicated that they possessed efficiency characteristics comparable with those of the aluminum alloys. The results of these tests are shown in Fig. 5.

Larger anodes were cast, analysing 1.37 per cent P, and a confirmatory run was conducted in 15 gallon (57 l) tanks. Early results continued encouraging, but after a few days, a large amount of tin-containing precipitate formed in the bath and, correspondingly, the tin content of the solution dropped suddenly. This phenomenon occurred again a few days later, and the experiment was abandoned. The precipitate was not further investigated; but it is known that stannous and stannic phosphates are highly insoluble.

Arsenic-tin.—Arsenic significantly improved the anode performance of tin anodes: slightly less than phosphorus in the potassium solution and slightly more in the sodium. The toxicity of arsenic and the possibility that it might plate out at the cathode ruled out its further consideration.

Antimony-tin.—One per cent Sb had negligible effect.

Bismuth-tin.—Bi (0.5 to 1.7%) had about the same effect as arsenic and phosphorus, and would have the same drawbacks as arsenic for practical application. The series, P-As-Sb-Bi, again illustrates the lack of predictability of these results, antimony alone being without effect.

Chromium-tin.—The 1 per cent Cr alloy showed higher efficiencies than pure tin, though the advantage is not striking. This alloy was not tested in the Na-1 bath.

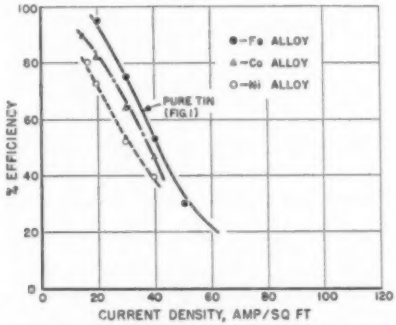

FIG. 6. Effect of iron, cobalt, and nickel on anode efficiency of tin in K-1 at 90 C

Manganese-tin.—Mn alloys ranging in composition from 0.6 to 1.7 per cent Mn were tested. They were significantly better than tin in both baths, and exhibited the interesting property that the stability of the anode film was notably improved: that is, the film persisted much longer after the current was shut off.

Iron-tin.—One per cent iron had negligible effect.

Cobalt-tin.—Cobalt was somewhat deleterious.

Nickel-tin.—One per cent Ni had a pronounced passivating action upon tin anodes. In the case of the series, Fe-Co-Ni, a regular trend was observed, as indicated in Fig. 6.

Summary of exploratory experiments

The twenty-six elements tested as alloying additions to tin anodes may be grouped into three categories, according to whether they increased or decreased the anode efficiency or had relatively little effect. It should be mentioned that because the determinations of anode efficiencies in short-time experiments are subject to fairly large errors, differences of less than 10 per cent or so in efficiencies were not considered significant.

These elements had a significantly beneficial effect upon anode performance: aluminum, gallium, phosphorus, bismuth, arsenic, manganese,

chromium, lithium, germanium, and sodium—the last only when the alloy was freshly made.

Negligible or minor in effect were: magnesium, mercury, antimony, calcium, iron, lanthanum, lead, zinc, and gold.

Having a definitely passivating action were: copper, thallium, silver, cobalt, indium, nickel, and cadmium.

Ternary alloys

A few ternary alloys were tested, to determine whether the effects of individual elements might be additive. The following were investigated (tin is the third constituent in each case): Al-As, Al-Bi, Al-Pb, Al-Mg, Al-Mn, Al-P, and Mg-Mn. In no case was the performance any better than that of binary Al-Sn alloys.

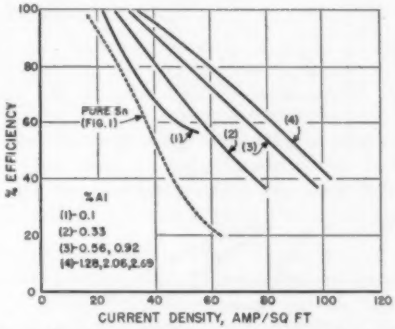

FIG. 7. Effect of aluminum on anode efficiency of tin in K-1 at 90 C

Aluminum-tin alloys

As already indicated, the most interesting results of this investigation, at least from a practical standpoint, concern the alloys of tin with small amounts of aluminum. Whereas the aluminum alloys, in the exploratory work, were better than any others in regard to anode efficiency, that is not the only reason for this interest. Some of the other alloying elements, phosphorus, arsenic, bismuth, and gallium, appeared almost as good. But aluminum combines with this anode performance the advantageous qualities of nontoxicity, economy, ease of alloying, favorable mechanical properties of the resulting alloy, and a position in the electromotive series which assures that it will not codeposit with tin at the cathode, in addition to filming characteristics discussed below. This combination of properties is shared by none of the other alloys tested.

Eight Al-Sn alloys were tested in bath K-1, to determine the optimum ranges of Al concentration. These contained 0.1, 0.33, 0.56, 0.92, 1.28, 2.06, and 2.69 per cent of Al. The results of the anode efficiency tests are shown in Fig. 7. It will be noted that as little as 0.1 per cent Al improves the anode performance slightly, but that, to gain the greatest effect, about 1 per cent of the Al should be used. Further increase in Al content confers no additional benefit, a fact which was further proved by experiments on alloys containing 5 and 10 per cent Al (not shown in the curve).

The same Al alloys were tested in the sodium bath, Na-1, with results summarized in Fig. 8. The improvement over pure tin is not so striking as in the potassium bath, but it is, nevertheless, definite.

The effect of aluminum on tin anodes was checked in potassium stannate baths ranging in tin content from 28 to 85 g/l, in free KOH from 9 to 52 g/l, and in solutions with 100 g/l added K_2CO_3. The temperature range

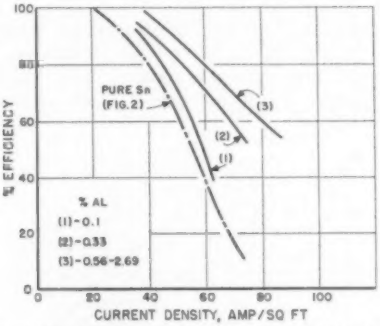

FIG. 8. Effect of aluminum on anode efficiency of tin in Na-1 at 90 C

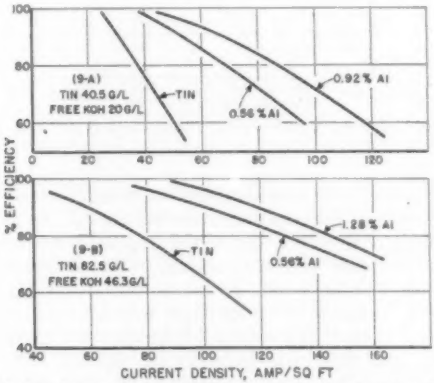

FIG. 9. Effect of aluminum on anode efficiency of tin in potassium stannate solutions at 90 C.

from 50 C to 90 C was also investigated. (It is not meant to imply that all Al alloys were checked in all solutions at all temperatures; a representative sampling of conditions was used.) Although the extent of the improvement over pure tin varied somewhat, it was in all cases appreciable, leading to the following generalization:

In any given potassium stannate plating solution, if pure tin anodes operate satisfactorily at a current density of X amperes per square foot, a 1 per cent Al-Sn alloy anode will operate at about the same anode efficiency at NX amperes per square foot where $N = 1.7$ to 3.0.

Confirmatory tests

Aluminum-tin alloy anodes were tested over a period of several months in 15-gallon (57l) tanks, with periodic analyses of the solutions being run as a check on the determination of efficiency by anode weight loss. These anodes have also been subject to trial by independent observers. No significant differences from their behavior on a laboratory scale were found during these extended tests. The aluminum content of the solution tends to build up to a low but constant value, above which the aluminum appears to sludge out. It is not possible to say just what this aluminum content of the solution will be in any given case; at any rate, no harmful effects of any kind were noted from the aluminate ion in the solution, and cathode tin tested spectrographically was shown to be free of aluminum.

Anode filming characteristics

It is well known that for proper operation of an alkaline stannate bath, either potassium or sodium, the tin anodes must be in a filmed condition. If no film is present, the anodes dissolve as bivalent tin or stannite ion, which, if present in appreciable amounts, produces spongy and nonadherent deposits. In order to form this film, the anodes must momentarily be subjected to a higher current density than the normal or operating current; after this surge has formed the film, as indicated by a sudden increase in the cell voltage, the current is then decreased to the correct operating value.

The current density required to form the film initially is called the critical anode current density (10). This critical current density (ccd) normally is about 50 to 70 per cent higher than the operating current density (ocd). Usually this presents no problem, but in large installations the necessary surge of current may, in some cases, be excessive for the installed generating capacity. It is, therefore, interesting to note that the aluminum alloy anodes filmed at or even below their normal operating current density, so that no surge of current was ever required to film them. This was true of all the aluminum alloys tested and in all the tests, both laboratory and extended runs. This property was shared only by the gallium alloy.

The film on the aluminum alloy anodes was quite different in appearance from that on pure tin. It was considerably darker, approaching a light khaki color when the anodes were dissolving properly, and, while a tin anode tends to become black when passivated by too high a current, the aluminum alloys first developed a white film which finally changed to black at very high current densities.

Mechanical properties

In most electroplating applications, the mechanical properties of the anodes are not of major interest. Hanson and Sandford (5) have shown, however, that the tensile strength of tin is increased more than threefold by the addition of about 1 per cent of aluminum, and, in a few cases, involving very large anode castings, this may be of some importance.

No difficulty was ever encountered in melting or casting the aluminum alloys; this is said here because of statements in the literature (5, 7) to the effect that Al-Sn alloys are subject to cracking and even disintegration on exposure to moist air. No such effect was ever noted in any part of this

investigation. The alloys were cut, machined, sampled by drilling, etc., with no trouble. Some of the castings have now been standing in the laboratory atmosphere for five years, and thin sections have indeed become somewhat brittle, but larger castings are still perfectly sound.[2]

SUMMARY

No attempt has been made in this paper to present the detailed results of all the anode efficiency and other tests which were run with the various alloys in the different solutions, nor has there been any attempt to explain the results from a theoretical standpoint. From the practical angle, it is believed that the aluminum alloy (about 1% Al) tin anodes will prove useful in enlarging the range of utility of the potassium stannate bath, by bringing the anode efficiency more nearly into line with the already proved higher cathode efficiencies which this bath offers.

Some of the principal results are summarized in Table II, which shows

TABLE II. *Operating current densities for 90% efficiency (ocd), critical current densities (ccd), and R (ccd/ocd) for tin and tin alloys in baths K-1 and Na-1 at 90C*

Alloying element	Bath K-1			Bath Na-1		
	ocd (amp/ft²)	ccd (amp/ft²)	R	ocd (amp/ft²)	ccd (amp/ft²)	R
Pure tin	23	39	1.7	31	41	1.3
Lithium	35	46	1.3	36	49	1.4
Sodium (fresh)	37	43	1.2	36	41	1.1
Copper	16	43	2.7	27	39	1.4
Silver	14	40	2.9	25	38	1.5
Gold	23	—	—	—	—	—
Magnesium	27	60	2.2	38	48	1.3
Calcium	23	41	1.8	31	40	1.3
Zinc	22	40	1.8	29	41	1.4
Cadmium	10	39	3.9	12	37	3.1
Mercury	24	41	1.7	31	37	1.2
Aluminum	44	40	0.9	48	41	0.9
Gallium	40	40	1.0	48	40	0.8
Indium	13	36	2.8	12	38	3.2
Thallium	18	43	2.4	20	38	1.9
Lanthanum	23	—	—	—	—	—
Germanium	34	43	1.3	41	42	1.0
Lead	23	42	1.8	37	38	1.0
Phosphorus	43	45	1.1	38	43	1.1
Arsenic	28	45	1.6	42	40	1.0
Antimony	23	44	1.9	32	40	1.3
Bismuth	33	48	1.5	39	42	1.1
Chromium	31	—	—	—	—	—
Manganese	27	41	1.5	38	40	1.1
Iron	23	40	1.7	31	41	1.3
Cobalt	15	—	—	—	—	—
Nickel	12	40	3.3	23	39	1.7

[2] Aluminum is said to promote the phase transformation of tin at low temperatures ("tin pest"). This may be true, but no practical difficulty has ever been encountered from this source.

the behavior of the various alloys in the two baths: potassium stannate, K-1, and sodium stannate, Na-1, at 90 C. In this table, the operating current density, ocd, is taken as the current density at which the anode efficiency is 90 per cent. The critical current density is that at which the anode first films, and the ratio, R, is ccd/ocd. A low value of R connotes that less excess current is required to form the anode film.

It should be understood that the values in the table are merely representative. If solutions of different compositions had been chosen, or if an anode efficiency of say 80 per cent had been considered satisfactory, different values would have been obtained. Nevertheless, the table may be useful in offering a quick summary of the results of this investigation.

CONCLUSIONS

The effect of twenty-six elements on the anodic behavior of tin in alkaline stannate baths has been shown. From a practical standpoint the aluminum alloys are of principal interest: about 1 per cent Al markedly improves the anode efficiency, thereby extending the range of usefulness of potassium stannate electrolytes. Other minor additions to tin also appear to have some beneficial effects, but all except aluminum have some drawbacks. It has also been shown that small amounts of some metals, notably cadmium, indium, and nickel, have strong passivating action and should by all means be avoided in tin anodes.

The aluminum-tin alloy anode has been subjected to sufficient testing to warrant recommending its commercial application.

Any discussion of this paper will appear in the discussion section of volume 96 of the TRANSACTIONS of the Society.

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ELECTROLYTIC REDUCTION OF ORGANIC COMPOUNDS

V. Cathodic Initiation of Vinyl Polymerization in Acrylic Acid, Methyl Acrylate, and Methacrylate. Carbonyl Reduction in Crotonic Acid[1]

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ABSTRACT

The behavior of acrylic acid and its methyl ester, methyl methacrylate, alpha-chloroacrylic acid, and crotonic acid in a sulfuric acid electrolyte at a mercury cathode is described. Dimeric products are not obtained. Reduction to dihydro-compounds is slow and difficult, but with acrylic and methacrylic derivatives polymerization is rapid. It is shown that this is a result of the cathodic process.

Some other metals as cathodes, Pb, Sn, Pt, Bi, Fe, Al, also cause polymerization. A radical mechanism is proposed.

Chloroacrylic acid loses most of its chlorine and gives a little acrylic acid polymer and propionic acid.

At both lead and mercury cathodes crotonic acid is reduced to butyric acid together with butyl alcohol and crotyl alcohol. The mechanism of this unusual reduction is discussed.

INTRODUCTION

It is now fairly well recognized that, in reduction using cathodes other than the catalytically active metals, only a carbon-carbon double bond conjugated with a carbonyl group is reducible. It would be convenient to reserve the term *electrolytic (or cathodic) reduction* for these instances and *electrolytic (or cathodic) hydrogenation* for those cases involving prepared nickel and platinum cathodes at which any carbon-carbon double bond may be reduced, just as if hydrogen and a catalyst had been used (1). This will be done in the present paper.

In electrolytic reduction, the susceptibility of the activated double bond is undoubtedly to be sought in the attraction that the beta-carbon atom possesses for electrons, and this view has offered an explanation of the fact that, in the reduction of sorbic acid, the amount of bimolecular product seems to be determined by the magnitude of the hydrogen overvoltage. Only sorbic (2) and cinnamic acids (3, 4, 5) have hitherto received much attention, and the present work extends the survey to include acrylic acid, its alpha-chloro, alpha-methyl, and beta-methyl (crotonic acid) derivatives.

EXPERIMENTAL

Materials

Acrylic acid.—Acrylonitrile was hydrolyzed in the presence of hydroquinone and copper (23) and the product flash distilled from a flask at

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250 C in the presence of bright copper wire to give a 52 per cent aqueous solution. A commercial product (60%, Rohm and Haas Company) stabilized with hydroquinone was also used either as received or after flash distillation.

Methyl acrylate and methacrylate.—The esters were commercial products (Rohm and Haas Company) containing hydroquinone (0.1%). They were distilled, bp 80.0–80.2 C and 100.4–101.0 C, respectively, from an all-glass still before use.

alpha-Chloroacrylic acid (24).—A cooled solution of paraformaldehyde (90 g) in water (54 g) and sulfuric acid (98%, 552 g) was added slowly to trichloroethylene (396 g) contained in a 3 liter, 3 neck flask fitted with stirrer, thermometer, and reflux condenser. One hour after hydrogen chloride ceased being evolved, the product was diluted with water (540 cm^3) and the chloroacrylic acid removed by steam distillation. The product (173 g, 60%) extracted from the distillate by ether and recrystallized from petroleum ether melted at 64–65 C.

Crotonic acid.—A commerical product (Tennessee Eastman Corporation) was recrystallized twice from petroleum ether, mp 71.5–72.0 C.

Mercury.—This was cleaned by drawing air through it while covered with a layer of nitric acid (4*N*) for three hours and used after washing. Occasionally the treatment was supplemented by vacuum distillation.

Lead.—A specimen containing less than 0.001 per cent of other metals was used. Most of the other metals used as cathodes or anodes were the purest obtainable from the usual supply houses.

Current was supplied by batteries or by a transformer through a rectifier. No variations in the course of reduction have been traced to differences in supply.

Apparatus

Reduction cells were of four different kinds:

(*a*) For large scale work reductions were carried out in cylindrical jars (1 liter) having a horizontal cross section of 100 cm^2. The anode compartment was a filter thimble (13 x 2.8 cm, Coors Porcelain Company, Catalogue No. 730). The anode was usually lead. Attempts were made to use diaphragms of filter paper and glass wool supported on glass tubes; these, however, proved unsatisfactory. The thimbles were cleaned before use by boiling with concentrated nitric acid. Cooling, when necessary, was provided by glass spirals. The jars were covered with loose fitting Plexiglas lids with holes for the various accessories. During prolonged reductions, where danger of loss of volatile materials existed, the lid was made tight with a rubber flange and provided with a gas outlet which was connected to a trap cooled in dry ice. Loss of product could thus be checked.

(*b*) Some experiments using a mercury cathode were carried out in a 3 neck flask having an extra side arm for contact with the cathode. The two outermost necks carried filter sticks (1.6 x 16.3 cm, Coors Porcelain Company, Catalogue No. 735) fastened in with rubber and the center neck held a condenser, used also as a gas outlet, and a stirrer. The gas outlet was connected with a dry ice trap.

(*c*) Preliminary scouting experiments with various metal anodes and cathodes were carried out in test tubes (0.5 x 3.0 in.) (1.3 x 7.6 cm). The electrodes were separated by a strip of glass. Visual observation was made

of the start of polymerization in relation to the electrodes. These experiments were considered only preliminary to be confirmed by those under (*d*).

(*d*) Polymerization studies were best made in the three compartment cell already described. The cell was set up in a thermostat maintained at 50 C.

Isolation and estimation of products

Acrylic acid.—Polymer was filtered off, washed with water, dried, and weighed. Methyl acrylate polymer was washed also with methyl alcohol. After separation of acrylic acid polymer, the residual electrolyte was extracted repeatedly with ether and the extract dried over magnesium sulfate. The residue contained only water and propionic acid, identified by its boiling range, 140–142 C, and the mp of its anilide, 106–107C. Its melting point when mixed with an authentic specimen, mp 105–106 C, was 105–106 C. No adipic acid was found in the propionic acid residue after distillation.

Using a sulfuric acid electrolyte (25%, 10 cm^3) and acrylic acid (52%, 100 cm^3), polymerization was evident after four hours using a current density of 0.1 amp/dm^2 at mercury. Ni, Al, Fe, and Cu gave no polymer.

With mercury and sulfuric acid (20%) containing acrylic acid (0.11 g/cm^3) and a current density of 1.0 amp/dm^2, propionic acid (6% yield) and polymer (78%) were obtained. At 0.02 g/cm^3 acrylic acid, the figures were 25 and 45 per cent, respectively. Neither polymer nor reduction was obtained using mercury and a half-neutralized solution of acrylic acid.

Methyl acrylate.—Polymer was rapidly produced at mercury (current density 1.0 amp/dm^2) using an electrolyte of sulfuric acid (20%, 124 g) and methyl alcohol (80 cm^3) containing methyl acrylate (40 g). After 20 hours, the polymer weighed 18.6 g. An experiment showing that polymerization did not occur at 70 C in absence of current was carried out in apparatus (*b*).

No polymer was obtained using an electrolyte of ammonium acetate, instead of sulfuric acid, with or without hydroquinone in the methyl acrylate.

Experiments with various electrodes in the three compartment cell (*c*) were carried out at 50 C. Polymer was never observed in the middle compartment. Current was usually 0.2 amp/dm^2.

Methyl methacrylate.—The ester (40 g), sulfuric acid (20%, 124 g), and methyl alcohol (80 cm^3) gave 54 per cent polymer in four hours at a current density of 3.0 amp/dm^2 using a cathode area of 10 cm^2.

alpha-Chloroacrylic acid.—Reduction was carried out in sulfuric acid (20%). Chloride ion was determined gravimetrically by acidifying with nitric acid and precipitating with silver nitrate. The precipitate was washed with ethyl alcohol and water, and dried. Ether extraction isolated as much as 30 per cent of the product as propionic acid. This was identified as p-bromophenacyl ester, mp 59–60.5 C, mixed melting point with authentic material (58–59.5 C) was 58–59 C.

In an experiment using mercury as cathode and chloroacrylic acid, 0.5 g/cm^3, propionic acid (30%), and acrylic acid polymer (chloride content, 2%) was obtained and 70 per cent of the chlorine was present as ion. With acrylic acid, 0.04 g/cm^3 chloride ion liberation was 84 per cent.

Crotonic acid.—In 20 per cent sulfuric acid at lead or mercury, an upper layer slowly accumulated. It gave no carbonyl reaction and distillation gave a fraction, bp 162–163 C, identified as butyric acid by preparation of the p-bromophenacyl ester, mp 64–64.5 C. The catholyte was thoroughly extracted with ether and the extract after removal of ether combined with the upper layer from the cell and refluxed with sodium hydroxide (30%). The alkali-insoluble alcohol fraction, bp 115–117 C, gave a 3,5-dinitrobenzoate, mp 46–54 C, which was raised by admixture with authentic *n*-butyl 3,5-dinitrobenzoate (mp 59–62 C). The alcohol fraction was unsaturated and a rough titration with bromine in chloroform (0.5*M*) showed it contained about 26 per cent unsaturation calculated as crotyl alcohol. Acetylation of the mixed alcohols and titration of the mixed alcohol acetates with bromine gave a figure of 27 per cent. Ultraviolet absorption after dilution with butyl alcohol gave a band at 264μ which was also given by authentic crotyl alcohol prepared by lithium aluminum hydride reduction of crotonaldehyde. Ozonolysis of the alcohol fraction gave acetaldehyde 2,4-dinitrophenylhydrazone, identified by mixed melting point. The amount corresponded with 20.0 per cent crotyl alcohol.

RESULTS

Acrylic and methacrylic acids.—Although both these acids have been known for a very long time, it is remarkable how little is recorded bearing on their reduction. Nobody, hitherto, appears to have studied their electrolytic reduction, but both sodium amalgam and zinc with acid, reagents which behave like cathodes, are stated to reduce these two acids, albeit with difficulty, to propionic (6) and isobutyric (7) acids, respectively. In the present experiments with acrylic acid, a mercury cathode and a sulfuric acid catholyte were used since these conditions should favor bimolecular product. Linnemann had already stated (6) that his reduction product from zinc and acid contained no adipic acid and we found this to hold also for a mercury cathode. The amount of propionic acid was small and, surprisingly enough, by far the major reaction was polymerization. Polymer formed even with a current density as low as 0.2 amp/dm^2. With the methyl esters of acrylic and methacrylic acids in a methanol-sulfuric acid electrolyte, polymerization was even more marked and little, if any, reduction occurred.

It appeared that polymerization was a direct result of the current flow since it did not occur if the current was not switched on even though the cell was heated for a long period of time. It apparently ceased, moreover, if the current was interrupted, since the amount of polymer formed remained constant for at least two hours afterward. At first, it was considered possible that polymerization might have been caused by peroxidic materials such as persulfate, which formed at the anode and diffused through the porous membrane into the cathode compartment. These peroxidic materials might then cause polymerization either directly or by reaction at the cathode in the manner of the well-known "reduction-activation" process. Appearances were against this since with a nonagitated catholyte polymer formed very rapidly after the current was switched on; moreover, it formed on the surface of the mercury cathode. Tests were made for peroxidic materials in the catholyte with potassium iodide, always without result. Polymeriza-

tion only occurred rapidly using a fairly strongly acid catholyte; it was very slow in weakly acid solution, and absent in neutral or alkaline solution. Moreover, if the composition of the catholyte was favorable, it proceeded even though the anolyte was made strongly alkaline. Persulfate does not form under alkaline conditions.

The most convincing demonstration that polymerization was the result of the primary cathodic process came from experiments with a specially designed cell shown in Fig. 1. It consisted of a wide glass tube sealed at each end and divided into three equal portions by two sintered glass disks. A condenser outlet was attached to each compartment and connections sealed to each end compartment for use with mercury electrodes. Owing to its easy polymerization, methyl acrylate in a methanol-sulfuric acid electrolyte was used and the same solution was placed in each of the three compartments, of which only the outer two carried electrodes. With mercury, polymerization at the cathode was rapid; but at the anode, also mercury, it was slow and accompanied by much corrosion. Nothing

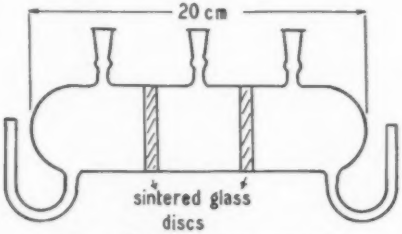


FIG. 1. Three compartment cell

at all happened in the middle compartment, no matter how prolonged the experiment. Besides mercury, only a few other metals (Pb, Sn, Pt, Bi, Fe, Al) caused polymerization when used as cathodes; many others (Cu, Cd, Ni, W, Ta, Mo, Cr, Ag, Zn) failed. In all cases current density was maintained as near 0.5 amp/dm^2 as possible. With a mercury cathode, polymerization occurred regardless of whether the anode was a metal (Hg, Pb, Cu, Cd, Pt) which itself gave polymer in its own compartment or was one (Fe, Ni, W, Mo, Bi, Sn, Ag, Zn) which did not. Most anodes were extensively corroded. It is clear from this that polymerization proceeds at the cathode irrespective of what happens at the anode and it is extremely unlikely, therefore, that the catalyst for polymerization originates in the anode compartment. It is concluded that polymerization is induced by the primary electron transfer or some process closely akin to it.

Mechanism of polymerization.—Free radical initiation is now widely held responsible for chain polymerization of vinyl compounds. A few cases are known, isobutylene for example, which give cationic chains but this type of process is usually limited to nonaqueous systems and it would seem necessary, therefore, to seek radical initiation in the present instance.

Since radicals have been postulated (1, 2, 3, 5) as intermediate in the formation of bimolecular products during electrolytic reduction of unsat-

urated compounds, it is natural to assume that the same entities are responsible also for polymerization. This may have provided the first convincing demonstration of their fleeting presence on the cathode (8). For some reason, at present unknown, the radical from acrylic acid, $\cdot CH_2CH_2CO_2H$, and that from methacrylic acid which presumably possess a beta-free valence, do not readily dimerize, since no trace of adipic or dimethyladipic acid could be found, but instead seek out monomer molecules and start polymer chains. If this is so, we should expect polymerization to be favored over reduction, the only other reaction by which radicals are destroyed, at high monomer concentrations. This was confirmed. With an acrylic acid concentration of 0.1 g/cm^3, the amount of polymer formed was roughly ten times that of propionic acid produced, while at 0.02 g/cm^3, they were approximately equal.

Since bimolecular product is controlled by overvoltage (1, 3, 5), polymerization should vary similarly if the same radical is concerned in both processes. This is partly confirmed by the list of metals in order of effectiveness (Pb, Sn, Hg, Pt, Bi, Fe, Al), which caused polymerization and those which failed (Cu, Cd, Ni, W, Ta, Mo, Cr, Ag, Zn). Except for the anomalous position of zinc and cadmium and of platinum and iron this list is quite compatible with a recent overvoltage sequence (9).

Peroxide catalyzed polymerization presumably begins by the attachment of a radical (probably hydroxyl) to the beta position, leaving the free valence on the alpha-carbon. This radical then attacks the beta position of a new monomer unit when propagation is the head to tail variety. In the cathodic process, the propagation is of the same kind, but initiation involves attack by the radical with a beta-, not alpha-free, valence. Thus (see below) only the start of the chain is different in the two polymerization processes.

$HO \cdot CH_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CH(CO_2H)$ (peroxide initiation)

$CH_2(CO_2H)CH_2 \cdot CH_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CH(CO_2H) \cdot CH_2 \cdot CH(CO_2H)$ (cathodic initiation)

Whether this can be shown by end group determination remains to be seen.

It is also possible, but rather improbable, that initiation in cathodic polymerization is caused by a radical produced by carboxyl group reduction. No sign of the corresponding reduction products has been detected although, as shown below, crotonic acid does undergo this type of reduction.

The addition of hydroquinone to the monomer did not inhibit cathodic polymerization in the slightest degree. It does, however, completely inhibit peroxide catalyzed polymerization in the concentrations used (0.1%). From this it would be concluded that the inhibitor reacts with the initiating peroxidic radical and not the growing chain.

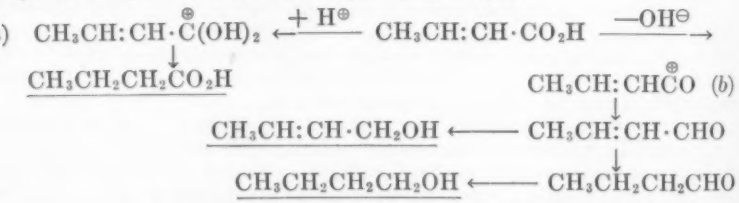
Crotonic acid.—Reduction of crotonic to butyric acid using hydrogen and a catalyst is well recognized (10, 11), and the equivalent electrolytic hydrogenation has been realized using a prepared nickel cathode (12). No previous record appears, however, of successful electrolytic reduction at noncatalytic cathodes; in fact, polarographic studies have indicated (13) that the acid is not reduced at mercury. Dissolving metals, such as

zinc in acid, and sodium amalgam, which are equivalent to cathodes, have been claimed to give butyric acid (14) but later workers (15, 16, 17) refuted this.

In the present experiments, using either lead or mercury cathodes, crotonic acid was reduced in a sulfuric acid electrolyte. The reaction was electrically inefficient requiring the passage of about ten times the theoretical amount of current for completion. The nature of the product was, however, unexpected since, in addition to butyric acid, about ten per cent was butyl alcohol and about two per cent an unsaturated neutral substance, probably crotyl alcohol. The alcohols were present after reduction as esters. Reduction of the carboxyl group is unusual and has been observed before only with benzoic, cinnamic, oxalic, and acetoacetic acids.

Crotonic acid gave no detectable dimer, thus resembling acrylic acid; neither did it polymerize, which is consistent with its stability in the presence of peroxides. In the course of the experiments, it was also shown that both butyric acid and the unsaturated alcohol were perfectly stable to further reducing action of the cathode, so that both alcohols must arise directly from crotonic acid, probably by way of crotonaldehyde. This intermediate has not yet been detected, but then it was some time, owing to its very low concentration, before benzaldehyde was detected in the reduction of benzoic acid (18).

Many of the reactions of carboxylic acids in the presence of sulfuric acid can be explained (19, 20) by the formation of two different carbonium ions. With crotonic acid, these are represented in the scheme below as (*a*), a dihydroxycarbonium ion formed by simple transfer of a proton from sulfuric acid to the carboxyl group, and (*b*), an oxocarbonium ion which results by loss of a hydroxyl ion from the carboxyl group. Since most carboxylic acids will undergo the simple proton transfer reaction to give (*a*), this ion can hardly be held responsible for carboxyl reduction, but only a few acids are supposed to yield an oxocarbonium ion and, in general, they are acids, such as 2,4,6-trimethylbenzoic (19, 20), in which there are special structural features which stabilize such an ion. Such features are also present in benzoic acid, cinnamic acid, and crotonic acid, due to conjugation with the benzene ring and hyperconjugation with the methyl group aided by a contribution from the carbon double bond. These are acids which undergo carboxyl reduction. Presumably the oxocarbonium ion abstracts an electron from the cathode to give first a radical then the aldehyde. Reduction of the latter, in the case of crotonic acid to butyl and crotyl alcohols, then follows an accepted pattern (3).



Reduction of crotonic acid (*products underlined*)

In the case of trimethylbenzoic acid (19, 20) evidence for the oxocarbonium ion comes not only from reactions, but also from depression of

freezing point of sulfuric acid solvent; it is, therefore, present in high concentration. In the acids under consideration, where structural features are less effective in stabilizing the carbonium ion, the concentration is undetectable by freezing point, but it need be only very small in order for the ion to be intermediate in reaction. It might be argued that the concentration of sulfuric acid in the catholyte is not high enough for oxocarbonium ion formation, but it should also be pointed out that, according to modern electrode theory, protons accumulate in the double layer, particularly at high overvoltage. As the sulfuric acid concentration was changed from 20 to 75 per cent, the ratio of butyric acid to alcohols produced remained sensibly constant. This could happen from the present hypothesis, since ions (*a*) and (*b*) are the result of acid-base equilibria, but sooner or later when the concentration of water can no longer be considered constant the oxocarbonium ion should increase relatively in concentration. This region must be in sulfuric acid concentrations above 75 per cent.

If crotonaldehyde is intermediate in alcohol formation from crotonic acid, then the ratio of the amounts of the two alcohols, butyl and crotyl, should be the same as that given by crotonaldehyde introduced as such into the cell. Information on this point is uncertain (21, 22), since the product is mainly dimeric, but it does correspond largely with carbon double bond saturation, that is, butyl not crotyl alcohol, just as found in the present experiments. The reason for dimeric and not monomeric products may be the result of operating at much higher crotonaldehyde concentrations than would obtain in the reduction of crotonic acid.

Finally, attention should be drawn to the series acetic, crotonic, and sorbic acids. The first has never been reduced electrolytically, although it has a methyl group and stabilization of an oxocarbonium ion by hyperconjugation is possible, the second is reduced in two ways, but the third undergoes only double bond reduction. It may be that hyperconjugation effects are at a maximum in crotonic acid, but the additional conjugation in sorbic acid is accompanied by dimerization. Many of these effects are still obscure.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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THE BEHAVIOR OF γ-KETO AND ALDEHYDO-ACID DERIVATIVES AT THE DROPPING MERCURY ELECTRODE

IV. Phthalaldehydic Acid Derivatives[1]

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ABSTRACT

In previous work, the polarographic method has been shown to be a suitable means of assigning structures to the derivatives of β-[p-bromobenzoyl] crotonic and 2-benzoylbenzoic acid derivatives with the exception of the anhydrides of 2-benzoylbenzoic acid. Additional data obtained from the study of phthaldehydic acid derivatives, the structures of which are well known, in unbuffered and buffered media indicate that 2-benzoylbenzoic anhydride and di-2-benzoylbenzoyl sulfide have normal structures, while the mixed anhydride from acetic acid and benzoylbenzoic acid has a cyclic structure.

INTRODUCTION

In previous work (1, 2), the use of the dropping mercury electrode in assigning structures to 2-benzoylbenzoic acid and β-(p-bromobenzoyl) crotonic acid derivatives has been successful in practically all cases except the anhydrides of 2-benzoylbenzoic acid (1). The results obtained with these compounds were difficult to interpret since the anhydrides hydrolyzed in the more alkaline buffer. In order to secure more data on compounds of this type, the work in this field has now been extended to derivatives of phthalaldehydic acid, an example of a γ-aldehydo acid. The structures in this series are well known since they can be determined easily by chemical means such as the Tollen's test or the fuchsin-aldehyde test.

EXPERIMENTAL

The current-voltage curves were determined in a manner similar to that described in the first paper in this series (1). All measurements were made in a water thermostat at 25 ± 0.1 C.

The dropping mercury electrode had the following characteristics. At a pressure of 70 cm of mercury, the drop time in the solvent used was 3.76 seconds (open circuit). The value of m was 1.32 mg sec^{-1} with a calculated value of $m^{\frac{1}{3}} t^{\frac{1}{6}}$ of 1.50 $mg^{\frac{1}{2}}$ $sec^{-\frac{1}{2}}$.

Materials

The solutions used had the following compositions and anode potentials:

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0.1*M* Tetrabutylammonium iodide in 50 per cent dioxane by volume, anode potential −0.400 volt.

Buffer I.—A mixture which was 0.172*M* tetramethylammonium hydroxide, 0.075*M* tetramethylammonium iodide, 0.102*M* phosphoric acid and 50 per cent dioxane by volume, anode potential −0.383 volt.

Buffer II.—A mixture which was 0.196*M* tetramethylammonium hydroxide, 0.075*M* tetramethylammonium iodide, 0.092*M* phosphoric acid and 50 per cent dioxane by volume, anode potential −0.366 volt.

Phthalaldehydic acid, phthalide, and benzaldehyde were obtained from stock. The normal alkyl esters (5), cyclic alkyl esters, diphthallyl ether (6), acetoxyphthalide (7), amide, anil (5), dihydrophthallyl (8), phthalimidine (9) and N-phenylphthalimidine (10) were prepared by appropriate methods given in the literature.

3-Phenoxyphthalide (cyclic phenyl ester).—Solid potassium phenoxide, prepared by heating potassium metal (6.9 g) with phenol (17.0 g) in absolute ether (200 ml) for two and one half hours, filtering, and washing with absolute ether, was added to a solution of chlorophthalide (10.7 g) in a mixture of dry benzene (100 ml) and absolute ether (400 ml) and the resulting mixture refluxed for five hours and then filtered. The filtrate after washing three times with 5 per cent sodium hydroxide and removing the solvent under reduced pressure gave a solid which could be separated into diphthalyl ether and the cyclic phenyl ester by treating with a limited amount of ether. The cyclic phenyl ester, which was more soluble in ether, after one recrystallization from this solvent and one from alcohol melted at 119–119.5 C (corrected); yield, 3.2 g. The ester gave negative tests with Tollen's reagent and the fuchsinaldehyde test.

Analysis calc'd. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46
Found: C, 73.93; H, 4.137.

RESULTS

The behavior of phthalaldehydic acid derivatives and related compounds was studied in both buffered and unbuffered media. A summary of the observed half-wave potentials and individual diffusion current constants is given in Table I.

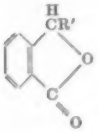
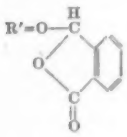
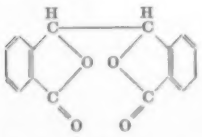
In general, the compounds gave well defined waves in unbuffered media and buffer II. In buffer I, waves at a potential more negative than −2.0 volts were difficult to measure because of their proximity to the residual current. The diffusion currents in this region were estimated by taking for their values the points at which the slope of the curves changed. Maxima could be suppressed in all cases except with phthalimidine by 0.001*M* methyl red or 0.01 per cent gelatin.

DISCUSSION OF RESULTS

An examination of the half-wave potentials of the esters and the anhydrides of phthalaldehydic acid in unbuffered solution indicates that they are reduced at the dropping mercury electrode to phthalide since they show a second wave with a half-wave potential (−2.05 v) similar to that of phthalide (−2.05 v). The reductions proceed in the same manner as in the 2-benzoylbenzoic acid series (1); the cyclic derivatives are reduced directly

TABLE 1. *Half-wave potentials and diffusion current constants for phthalaldehydic acid derivatives and related compounds in various solutions at 25 C*

0.1*M* Tetrabutylammonium iodide—50% dioxane

Compound	$E_{\frac{1}{2}}$ vs. S.C.E.* volts	i_d, micro-amperes	C, millimoles liter	$(i_d/cm)^{\frac{1}{2}}\ t^{\frac{1}{6}}$
Acid (R=H)	−1.08	2.16	1.15	1.25
	−1.55	2.02		1.17
	−2.11	.58		.34
n-Methyl	−1.35	3.32	1.15	1.92
ester ($R=CH_3$)	−2.07	4.18		2.42
n-Ethylester	−1.37	2.55	1.06	1.60
$R=CH_2CH_3$	−2.05	4.59		2.88
				
Phthalide	−2.02	8.05	1.37	3.91
R′=H				
ψ-Methyl	−1.89	10.97	2.39	3.27
ester	−2.02	5.42		1.52
$R=OCH_3$				
ψ-Ethyl	−1.89	8.74	2.05	2.84
ester R′=OC_2H_5	−2.00	4.67		1.51
ψ-Phenyl	−1.66	3.44	0.98	2.34
ester R′=OC_6H_5	−2.05	4.48		3.05
Acetoxyphthalide	−1.53	4.49	1.37	2.18
R′=$OCOCH_3$	2.06	5.11		2.48
Diphthalyl	−1.59	6.24	1.04	4.00
ether	−2.04	4.22		2.70
				
Anil	−1.10	1.34	.86	1.04
R′=NHC_6H_5	−1.56	1.75		1.36
	−2.10	.27		.21
				
Dihydrophthallyl	−1.91	0.98	1.22	3.81

* S.C.E. = Saturated calomel electrode.

TABLE I.—*Continued*

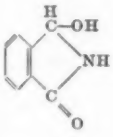
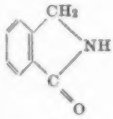
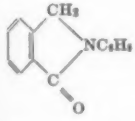
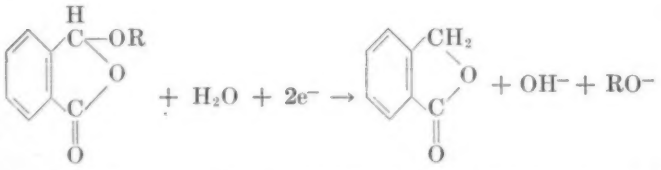
Compound	$E_{\frac{1}{2}}$ vs. S.C.E.* volts	i_d, micro-amperes	C, millimoles liter	$(i_d/cm)^{\frac{1}{2}} t^{\frac{1}{6}}$
	−2.01	7.19	1.85	2.58
Amide				
	Maximum			
Phthalimidine				
	−2.20	4.00	1.02	2.61
N-Phenylphthalimidine				
Benzaldehyde	1.54	9.77	5.42	1.20
Buffer I				
Acid	−1.38	4.96	1.37	2.41
n-Methy lester	−1.21	3.48	1.04	2.23
n-Ethyl ester	−1.22	2.38	.83	1.92
Phthalide	−2.05	8.24	1.29	4.25
ψ-Methyl ester	−1.90	3.37	1.00	2.25
ψ-Ethyl ester	−1.92	2.77	1.01	1.83
ψ-Phenyl ester	−1.73	2.78	0.90	2.06
Acetoxyphthalide	−1.58	2.77	0.90	2.06
Diphthalyl ether	−1.69	6.66	1.30	3.41
Anil	−1.16	2.09	0.88	1.58
	−1.40	0.60		0.45
Dihydrophthallyl	−1.92	4.03	1.06	2.53
Amide	−2.01	5.34	1.00	3.26
Phthalimidine	Max.			
N-Phenylphthalimidine	−2.14	11.59	1.00	7.74
Benzaldehyde	−1.46	4.66	1.46	2.12
Buffer II				
Acid	−1.49	4.74	1.45	2.18
n-Methyl ester	−1.46	2.76	1.04	1.77
n-Ethyl ester	−1.47	1.82	0.83	1.46
Phthalide	−2.05	7.61	1.29	3.92

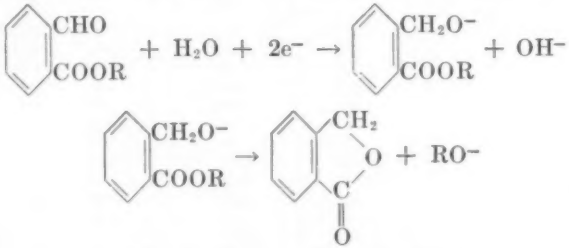
TABLE I.—*Concluded*

Compound	$E_{\frac{1}{2}}$ vs. S.C.E.* volts	i_d, micro-amperes	C, millimoles liter	$(i_d/cm)^{\frac{2}{3}} t^{\frac{1}{6}}$
		Buffer II—*Continued*		
ψ-Methyl ester	−1.88	3.98	1.00	2.66
ψ-Ethyl ester	−1.91	3.10	1.01	2.02
ψ-Phenyl ester	−1.71	2.48	0.90	1.83
Acetoxyphthalide	−1.51	2.88	0.90	2.14
Diphthalyl ether	−1.47	10.44	1.51	4.60
Anil	−1.15	0.45	0.89	0.34
	−1.45	2.49		1.86
Dihydrophthallyl	−1.52	0.59	0.66	0.60
	−1.71	0.56		0.57
Amide	−2.00	3.87	1.09	2.36
Phthalimidine	Max.			
N-Phenylphthalimidine	−2.15	17.24	1.00	11.50
Benzaldehyde	−1.53	4.45	1.11	2.67

* Saturated calomel electrode.



to phthalide and an alcohol or acid while the normal derivatives must be first reduced to the benzoyl alcohol and then lose ethyl or methyl alcohol



$$RO^- + H_2O \rightleftarrows ROH + OH^-$$

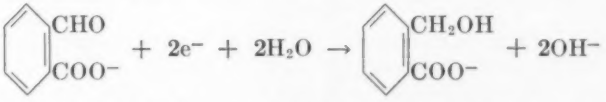
and form phthalide. The low diffusion currents obtained for the second wave of these compounds suggest that the reduction to phthalide is not quantitative but is accompanied by side reactions. The possibility that the diffusion currents in the case of the normal esters were low because of a bimolecular reduction and a loss of alcohol to form dihydrophthallyl, was ruled out by the more positive half-wave potential (−1.91 v) obtained for this compound and by its instability in buffer II.

Data obtained from the half-wave potentials in buffers I and II indicate that the esters and anhydrides can be divided into two classes. The first

class, which includes the cyclic esters and anhydrides, has curves with half-wave potentials which become more negative in going from unbuffered media to buffer I. In buffered solutions the half-wave potential for the cyclic esters are independent of pH. A similar comparison can not be made for the anhydride, since they hydrolyze in buffer II and give waves similar to those obtained for the acid. The ease of reduction in this series increases with the ionization constant of the alcohol, phenol, or acid involved in a manner to that observed with the cyclic derivatives of 2-benzoylbenzoic acid (1). In this comparison using ionization constants, it is surprising that the cyclic anhydride, diphthalyl ether (−1.69 v), is only slightly more easily reduced than the cyclic phenyl ester (−1.73 v).

The second class which contains the normal methyl and normal ethyl esters shows a decrease in half-wave potentials in going from unbuffered media (−1.35 v) to buffer I (−1.22 v). Only about half this change is observed with benzaldehyde (0.08 v). In the more alkaline buffer II, both esters are saponified since waves are obtained similar to those for the acid. This behavior parallels that observed with the normal esters of 2-benzoylbenzoic acid, 2-benzoylbenzoic anhydride, and di-3-phenylphthalyl sulfide and indicates a normal structure for the two anhydrides. The last compound is, therefore, really di-2-benzoylbenzoyl sulfide. Since acetic 2-benzoylbenzoic anhydride gives a wave with a half-wave potential (−1.48 v) more negative than that (−1.28 v) of 2-benzoylbenzoic anhydride in unbuffered media, a behavior which is exactly opposite to that observed with the corresponding cyclic phthaldehyde acid derivatives, the former must have a cyclic structure. These structures of 2-benzoylbenzoic anhydride and 3-acetoxy-3-phenylphthalide are in agreement with recent ultraviolet absorption spectra work upon these compounds (3).

Phthalaldehydic acid in unbuffered media behaves as an equilibrium mixture of the normal and cyclic forms. The wave at −1.08 volts is due to the reduction of the unionized normal form, while that at −1.55 volts is for the reduction of the ionized normal form. The wave at −2.11 volts suggests a reduction of the ionic cyclic form since it is more negative than the wave for phthalide. In buffered solution the acid is apparently present mainly



as the open anion since a wave which is more negative than that of the normal esters and which changes with pH is obtained. Such structures are in agreement with ultraviolet absorption data (4).

The behavior of the amide at the dropping mercury electrode indicates a 3-hydroxyphthalimidine structure since only one wave at −2.01 volts was obtained. No reduction wave for the resulting phthalimidine was observed because this compound gives a maximum. A 3-aminophthalide structure would give rise to a wave for the reduction of phthalide.

The anilide shows a behavior which resembles that of phthalaldehydic acid and the anil in the 2-benzoylbenzoic acid series, and must, therefore, exist as an equilibrium structure between the acid and 3-anilinophthalide. This structure is confirmed by the chemical reactions reported (5) and by

the absence of a wave for N-phenylphthalimidine. The latter would result if a 2-phenyl-3-hydroxyphthalimidine structure were present.

SUMMARY

1. The polarographic method provides a suitable means for distinguishing between the open and cyclic forms of phthalaldehydic acid and its derivatives.

2. The data obtained indicate normal structures for 2-benzoylbenzoic anhydride and di-2-benzoylbenzoyl sulfide and a cyclic structure for the mixed anhydride from 2-benzoylbenzoic acid and acetic acid.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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PERFORMANCE OF ELECTROLYTIC CELLS IN THE REDUCTION OF GLUCOSE[1]

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Atlas Powder Company, Wilmington, Delaware

ABSTRACT

A description is given of the cell used for the reduction of glucose on a commercial scale. Data are presented to show the effects of varying current density, initial sugar concentration, ratio of cathode area to volume of catholyte, alkalinity of catholyte, and temperature. The first three of these variables may be combined as weight of initial sugar per ampere. The instantaneous rate of reduction is discussed. The limiting rate of reduction is proportional to the concentration of sugar in the catholyte. Magnesium behaves as a cathode poison.

INTRODUCTION

The electrolytic reduction of glucose has been carried out on a commercial scale for approximately twelve years. The process is a very interesting one because by proper control of operating conditions it is possible to produce several polyols and to regulate their proportions in the product. The usual products are sorbitol, mannitol, and a noncrystallizing mixture of sorbitol and closely related polyols. The process can be operated to produce a noncrystallizing syrup which contains very little sorbitol and no recoverable mannitol. The development of the process and the chemistry of the reactions which take place have been admirably presented by Creighton (1, 2), who pioneered in the work. In reporting their studies of electrolytic reduction of hexoses, Parker and Swann (3) review the relevant literature and patents. The plant built in 1937 by Atlas Powder Company has been described by Killeffer (4) and by Taylor (5). The problems attendant to the operation of electro-organic processes have been discussed by Swann (6).

PROCESS

The commercial process for the electrolytic reduction of glucose is performed batchwise. The catholyte is an aqueous solution of glucose and sodium sulfate with or without sodium hydroxide depending upon the product to be made. The anolyte is dilute sulfuric acid. The anode is lead and the cathode is amalgamated lead (7) or amalgamated zinc (8). The catholyte and anolyte are separated by a diaphragm.

When reduction of a batch of catholyte has been completed, the catholyte is removed from the cell system. The reduced catholyte is neutralized, filtered, and evaporated nearly to dryness. Most of the sodium sulfate crystallizes during the evaporation step. The residue in the evaporator is digested with hot aqueous ethanol and the slurry is filtered to remove the sodium sulfate. If mannitol is present, the filtrate is cooled. The mannitol crystallizes and is separated from the ethanolic solution of sorbitol (9).

[1] Manuscript received May 24, 1949. This paper prepared for delivery before the Chicago Meeting, October 12 to 15, 1949. Published by permission of the Atlas Powder Company, Wilmington, Delaware.

The ethanol is separated from the sorbitol by distillation. The still residue is an aqueous solution of sorbitol. It is treated to remove color and other impurities, then adjusted to the proper concentration for packaging. The mannitol is purified by recrystallization from water.

REDUCTION CELL AND ASSOCIATED EQUIPMENT

A reduction unit consists of a cell, a tank, a cooler, and a circulating pump. The original commercial cell is a rectangular steel box 13 feet (3.96 m) long, 6 feet (1.83 m) wide, and 2 feet (0.61 m) deep which is lined internally with rubber. The diaphragms are ceramic boxes with open tops. These diaphragm boxes are 24 in. (61 cm) long, 24 in. (61 cm) deep, and 3 in. (7.6 cm) wide, outside. The anolyte is contained in the diaphragm boxes. The cathodes are hung between the diaphragm boxes. Each cell contains 36 cathodes, 35 anodes, and 70 diaphragms. The diaphragms are set in 35 rows of two each, and baffles direct the flow of catholyte back and forth across the cell past groups of diaphragms. Each anode has two skirts and serves a row of two diaphragms.

It is necessary to have the cathodes as close to the diaphragms as possible in order to reduce the power consumption of the cell, because of the electrical resistance of the catholyte. This restriction results in a cell with small holding capacity for catholyte. The purpose of the tank is to permit the use of the desired ratio of cathode area to catholyte volume and to take care of the expansion of the volume of catholyte during the run. The tank is at a lower elevation than the cell.

The cooler is required for the control of the catholyte temperature. The heat of reduction of dextrose to sorbitol (110 Btu per pound), the heat absorbed from the surroundings and the circulating pump, and the heat equivalent to the electrical energy used in the cell must be removed by the catholyte cooler. The catholyte cooler consists of glass pipes which are jacketed with steel pipes through which the cooling water flows. The glass pipes are set horizontally, one above the other, and are connected by rubber return bends.

The pump withdraws catholyte from the tank and forces it through the cooler to the cell box.

Fig. 1 shows the arrangement of the equipment.

It seems that a mercury surface is necessary for the production of mannitol and of sorbitol of high purity. The use of liquid mercury is practically out of the question economically. It has been found that amalgamated lead (7) and amalgamated zinc (8) are satisfactory cathode materials. Amalgamated zinc cathodes have no advantage over lead cathodes in reductions at high alkalinity, but their use results in more rapid reduction of glucose at low alkalinity. The subject of cathode materials has been discussed by Creighton (1). Parker and Swann (3) have reported the results of an investigation of a number of cathode materials for the reduction of hexoses.

The addition of zinc sulfate to the catholyte will cause a cathode of amalgamated lead to behave like one of amalgamated zinc (10).

The anodes are made of sheet lead. They soon become coated with a layer of lead peroxide.

The rate of circulation of the catholyte is determined by the permissible rise in its temperature as it passes through the cell box. The anolyte is not circulated.

At conditions of high alkalinity and high temperature, there was a tendency for a water insoluble deposit of some organic material to form on the cathode side of the diaphragms. This coating was removed by washing the diaphragm with a ketone.

Two types of laboratory cells were used. One consisted of a rectangular battery jar fitted with box-like diaphragms similar to those of the commercial cells and of the same composition and properties. The cathodes and anodes were flat plates. The catholyte was circulated by means of motor driven stirrers placed in the space behind the cathodes. The cell was immersed in a thermostat. The ratio of cathode area to volume of catholyte was controlled by varying the volume of the battery jar and the immersion of the cathodes.

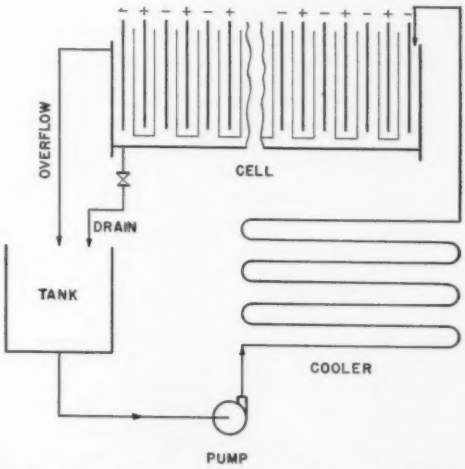

FIG. 1. Arrangement of reduction cell and associated equipment

The other type of cell was provided with an external tank to contain the excess catholyte. The tank was equipped with cooling coils. The catholyte was transferred from the tank to the cell by means of a hard rubber pump and returned to the tank by gravity flow.

Contact of the catholyte with air was minimized by covering the surface of the liquid with floats of sponge rubber or of paraffin, except in the space between the cathodes and diaphragms (19).

OPERATING CONDITIONS

The composition of the reduction product depends on the alkalinity (or acidity) of the catholyte, the temperature of the catholyte, the initial concentration of sugar, the ratio of cathode area to volume of catholyte, the current density, and the character of the cathode surface.

Very careful control of conditions is necessary, because the composition of the product is altered greatly by small changes in the value of some of

the variables, particularly the temperature and alkalinity of the catholyte and the nature of the cathode surface.

The usual values of the operating conditions fall within the following limits:

Current density	1 to 2 amp/dm²
Catholyte temperature	68 to 75 F
Ratio of cathode area to catholyte volume	0.8 to 2.5 dm²/l
Alkalinity of catholyte	Zero to 20 g NaOH/l
Initial sugar concentration	300 to 500 g/l
Sodium sulfate concentration	70 to 100 g/l

COMPOSITION OF CATHOLYTE

Since reduction takes place at room temperature, the concentration of dextrose is limited by its solubility to approximately 500 grams per liter of catholyte.

Sufficient sodium sulfate is added to give electrical conductivity for economical operation. One must balance the cost of current against the cost of separating the salt from the reduced catholyte.

Small amounts of aluminum, iron, nickel, or copper in the catholyte are tolerated by the cell. However, magnesium (11) and chromium must be absent. The effect of the concentration of magnesium on the rate of reduction will be shown later.

CURRENT DENSITY

The current density, like the concentration of sodium sulfate, is determined by economic considerations. Fig. 2 shows the relationship between the voltage of the cell and the current density. If the rate of reduction throughout the run corresponded to the current density, the use of high current density might seem desirable, in order to increase the productivity of the cells. However, the rate of reduction is not constant. The maximum possible rate of reduction is a function of the sugar concentration and the temperature. A high current density can be utilized only during the early portion of a run. This matter will be discussed again in connection with the rate of reduction.

RATE OF REDUCTION

Fig. 3, 4, and 6 are constructed from the same set of data. The operating conditions for the run were:

1. Cathodes, amalgamated zinc
2. Initial sugar concentration, 500 g/l
3. Cathode ratio, 1.21 dm²/l
4. Alkalinity, 10 to 20 g NaOH/l
5. Temperature, 69 F
6. Current density, 1 amp/dm²

Fig. 3 shows the relationship between the residual sugar concentration and the time of reduction.

The first portion of the curve is a straight line, showing that the rate of reduction is constant during the corresponding period of time. This initial constant rate period is followed by one of constantly decreasing rate.

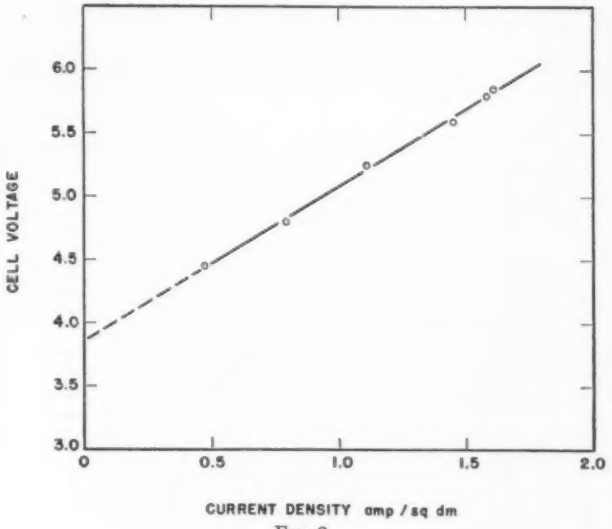

FIG. 2

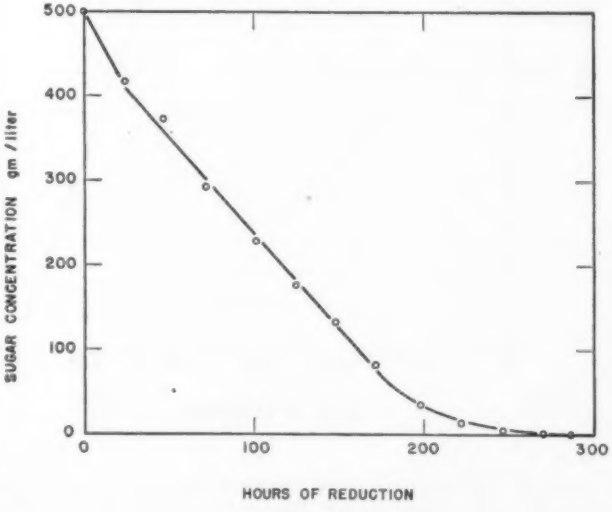

FIG. 3

A plot of the logarithm of the concentration of sugar *vs.* time for this falling rate period is a straight line, indicating that, during this period, the

rate of reduction is proportional to the sugar concentration. This is illustrated by Fig. 4.

The easiest way to show graphically the state of affairs is to plot the rate of reduction *vs.* sugar concentration. Fig. 5 diagramatically illustrates such a plot.

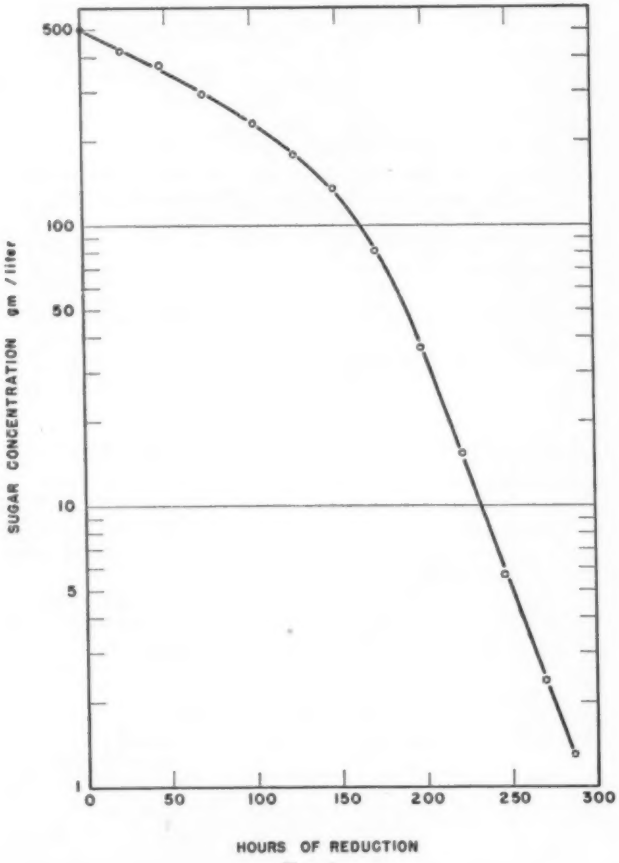

FIG. 4

Line segment *DB* represents the constant rate period and segment *OA* represents the falling rate period. The position of segment *DB* is determined by the current density and the current efficiency and that of *OA* by the temperature and the alkalinity of the catholyte and to some extent by the condition of the cathodes.

It is quite reasonable to expect that the maximum rate at which the sugar

RATE OF REDUCTION gm sugar / sq dm / hour

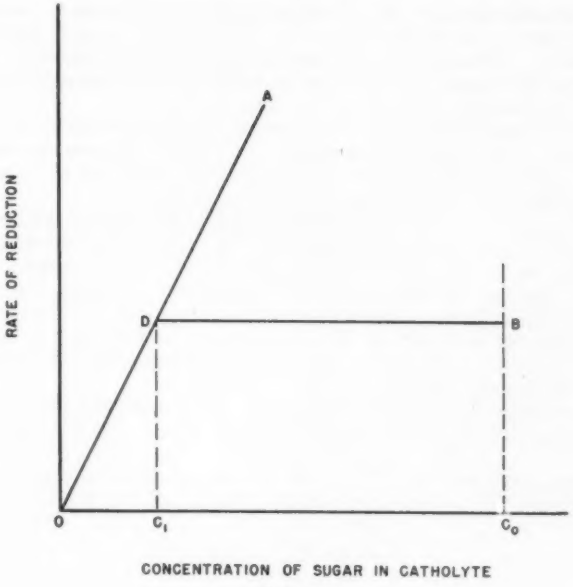
RATE OF REDUCTION
A
D
B
O
C_1
C_0
CONCENTRATION OF SUGAR IN CATHOLYTE

FIG. 5

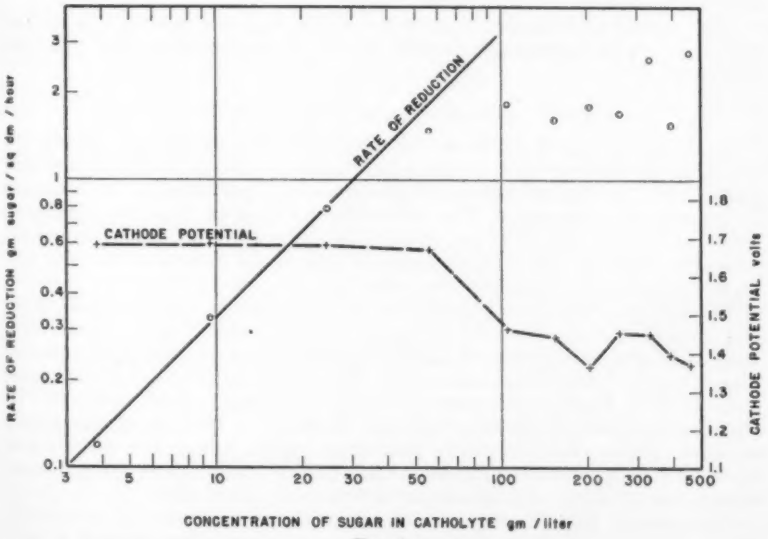
RATE OF REDUCTION gm sugar / sq dm / hour
CATHODE POTENTIAL volts
RATE OF REDUCTION
CATHODE POTENTIAL
3
2
1
0.8
0.6
0.4
0.3
0.2
0.1
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
3
5
10
20
30
50
100
200
300
500
CONCENTRATION OF SUGAR IN CATHOLYTE gm / liter

FIG. 6

can be reduced will be proportional to its concentration in the bulk of the catholyte, since it must diffuse through the stagnant layer of liquid on the surface of the cathode before it can be reduced. The matter of so-called limiting current density and its relation to the concentration of depolarizer has been discussed by Glasstone and Hickling (12).

The use of logarithmic scale cross section paper is preferred for the plotting of rate of reduction *vs.* concentration of sugar because the concentration scale is contracted at high values of concentration and because the line corresponding to *OA* will always have a slope of unity.

Fig. 6 is a plot of experimental data on logarithmic scale coordinate paper. The rates at high values of concentration seem somewhat erratic, but this is probably due to the use of small differences of large numbers in determining the amount of sugar reduced. The logarithmic mean of the concentrations at the beginning and end of a period of time is used as the average concentration for that period. This is necessary in the case of the line of limiting rate and introduces no error in the ordinate of the line representing the constant rate period.

Fig. 5 explains why the use of a high current density may be undesirable economically. The higher the current density, the shorter is the time it can be utilized.

The slope of the line *OA* in Fig. 5 or the intersection of the 45° line in Fig. 6 with the line $C = 1$ (i.e., $\log C = 0$) is the value of K in the rate equation:

$$-\frac{1}{R} \cdot \frac{dC}{dt} = KC \qquad \text{(I)}$$

where R is the ratio of cathode area to volume of catholyte and C is the volumetric concentration of sugar.

Fig. 7 shows the effect of magnesium on the rate of reduction. The apparent delay in its action is proabably due to the time required for it to coat the cathode.

ALKALINITY, CATHODE RATIO, AND CURRENT DENSITY

In the reduction of dextrose, the alkalinity of the catholyte affects the character of the products. It has been shown by Lobry de Brun and Van Eckenstein (13) that alkali causes glucose, in aqueous solution, to isomerize to fructose and mannose. The reduction product of glucose is sorbitol. Fructose reduces to a mixture of sorbitol and mannitol, and mannose reduces to mannitol. An alkaline aqueous solution of glucose, therefore, will form sorbitol and mannitol upon reduction.

The action of alkali on glucose can be more far reaching, however, than the formation of fructose and mannose. A review of the action of alkali on the hexose sugars is presented by Evans in his paper concerning the mechanism of carbohydrate oxidation (14). Wolfrom (15) and co-workers have isolated D-L-glucitol, 1-desoxy D-mannitol (D-rhamnitol), 2-desoxy D-mannitol (2 desoxysorbitol), allitol, a 2-desoxy hexitol of undetermined configuration, and a pentitol of unknown structure from the products of the electrolytic reduction of glucose. Goepp and Soltzberg (16) have demonstrated the presence of a substance having a branched chain.

It is evident that the sugar is transformed into a number of substances and that the composition of the product obtained from the cell will depend

upon the relative rates of the transformation reactions and the rate of reduction.

The sorbitol content of the reduction products can be determined by the use of pyridine (17). Under suitable conditions, this substance forms an

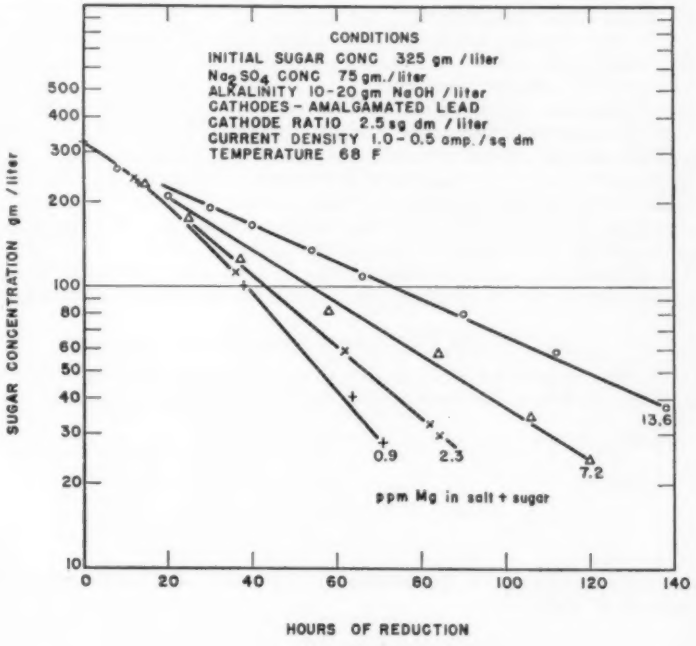

FIG. 7

TABLE I. *Effect of alkalinity and cathode ratio*

	Ratio, dm²/l					
	1.25		2.5		7.8	
	P.N.	*% Man.*	*P.N.*	*% Man.*	*P.N.*	*% Man.*
Alkalinity, 0-2 g NaOH/l	79	0	82	0	84	0
9-11 g NaOH/l	62	13.5	64	2.2	82	0
19-21 g NaOH/l	51	19.5	60	12	78	0

insoluble complex with sorbitol. In this discussion, the term Pyridine Number (P.N.) will indicate the amount of sorbitol which can be separated from a sample by means of this reagent, expressed as the weight per cent of that portion of the sample which remains after the removal of any crystallizable mannitol.

The temperature of the catholyte influences the rate of isomerization,

and the effects produced by alkali may be produced to some extent merely by sufficient increase in the temperature of the catholyte.

Table I illustrates the effects on the products of reduction of alkalinity and of the ratio of cathode area to volume of catholyte. The other operating conditions were:

1. Initial sugar concentration, 325 g/l
2. Current density, 1.0 then 0.5 amp/dm² after 67% reduction
3. Temperature, 68 F
4. Cathodes, amalgamated lead

The cathode ratio of 7.8 dm²/l was obtained by placing the catholyte within the diaphragms and the anolyte outside them. The symbol "% Man." represents the amount of crystallizable mannitol in the product.

In general, the yield of mannitol increases with increasing alkalinity and decreases with increasing value of cathode ratio. The P.N. increases with decreasing alkalinity and increasing cathode ratio, i.e., with decrease in opportunity for the transformation of the sugar by alkali.

The effect of increasing current density is to shorten the time the sugar is exposed to the action of alkali and hence is to lower the yield of mannitol

TABLE II. *Effect of current density*

Conditions: temperature, 90 F; cathode ratio, 1.21 dm²/l; initial sugar concentration, 500 g/l; catholyte alkalinity, 10–20 g NaOH/l; cathodes, amalgamated lead.

Current density, amp/dm²	% Mannitol	P.N.
4	19.5	35.5
6	16.1	34.0
8	14.7	45.0

and increase the P.N. of the nonmannitol portion of the product. This is illustrated in Table II.

TEMPERATURE OF THE CATHOLYTE

The effect of increasing the temperature of the catholyte is to increase the rate at which alkali acts on the sugar. It should be similar, therefore, to the effect of increasing the alkalinity of the catholyte in that the P.N. of the product will decrease. The effect of temperature is illustrated by Table III.

Increase of temperature also increases the rate at which sugar can reach the cathode by diffusion through the film of liquid about it and hence increases the value of K in equation (I).

It is possible to alter the value of one variable to compensate for a change in another. For example, an increase in current density will compensate for an increase in temperature as far as the yield of mannitol and P.N. of the syrup are concerned. Such data are shown in Table IV.

The length of time the sugar is exposed to alkali in the cell prior to reduction is a function of the initial sugar concentration, the ratio of cathode area to catholyte volume, the current density, and the current efficiency.

Let C = concentration of sugar, g/l

R = ratio of cathode area to catholyte volume, dm²/l

TABLE III. *Effect of temperature*

Conditions: initial sugar concentration, 325 g/l; cathodes, amalgamated lead; cathode ratio, 1.21 dm²/l; current density, 1.0 then 0.5 amp/dm² after 80% reduction; alkalinity, 10-20 g NaOH/l.

Reduction temperature, F	68	72	76	81
% Mannitol	18.2	19	14.3	1.2
P.N. of syrup	56.5	44.5	0	0
Color of syrup	Very light lemon	Water white	Dark brown	Very dark brown

TABLE IV. *Compensation for change of temperature*

Conditions: initial sugar concentration, 500 g/l; cathodes, amalgamated lead; cathode ratio, 1.21 dm²/l; alkalinity, 10–20 g NaOH/l.

Catholyte temperature, F	69	81	83	85
Current density, amp/dm²	1	4	5	6
% Mannitol	16	17.4	17	16.7
P.N. of syrup	42.5	40.5	41.5	38

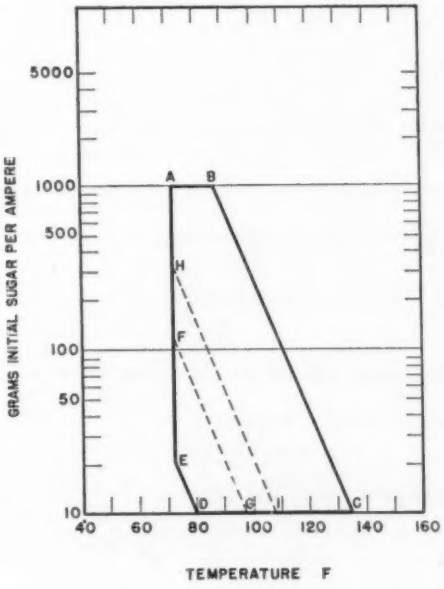

FIG. 8

D = current density, amp/dm²
E = current efficiency
T = time in hours
3.36 = grams glucose theoretically reduced by 1 amp-hr of electricity.

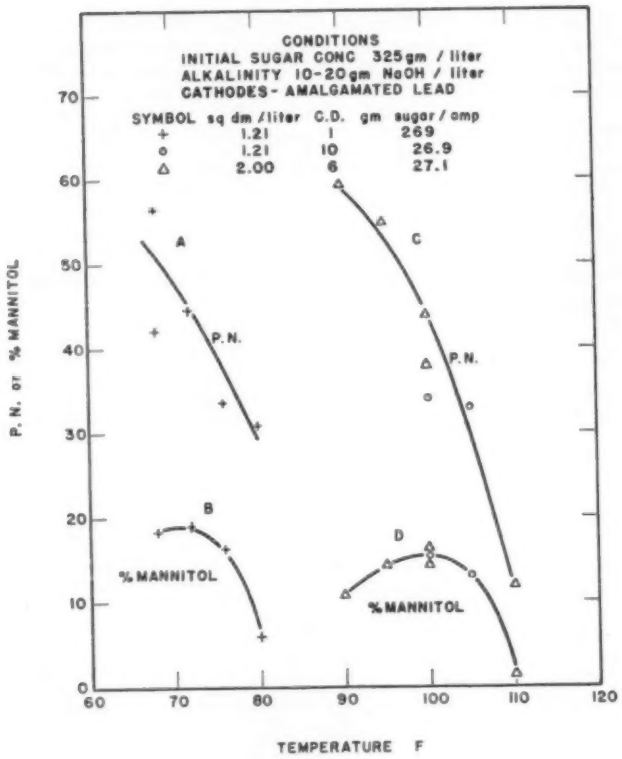

FIG. 9

In Fig. 5, the time to reduce the sugar concentration from C_0 to C_1 will be:

$$\frac{(C_0 - C_1)}{3.36\ RDE} = T \tag{II}$$

Let K = the slope of line OA in Fig. 5.

$$\text{then } C_1 = \frac{3.36\ DE}{K} \tag{III}$$

Substituting (III) in (II) there is obtained:

$$T = \frac{C_0 - 3.36\ DE/K}{3.36\ RDE} = \frac{C_0}{3.36\ RDE} - \frac{1}{RK} \tag{IV}$$

The group C_0/RD is equal to the ratio of the sugar initially present to the electric current, expressed as grams of sugar per ampere.

It has been found, empirically, that the group of variables $C_0/R \times D$ can be used in the control of the quality of the products of the reduction of glucose, and that for any specified alkalinity of catholyte, there is a relationship between the logarithm of the expression $C_0/R \times D$ and catholyte temperature, which will result in constant product composition. This relationship is the subject of a patent by Creighton and Hales (18). Fig. 8 is taken from the patent.

For any given set of conditions of sugar, catholyte alkalinity (or acidity), and cathode material, substantially the same product can be made at the ratios of temperature to grams initial sugar per ampere which lie on lines parallel to the line *BC*. For example the line *FG* represents the relationship between temperature and grams of initial sugar per ampere for making high purity sorbitol from glucose with an amalgamated zinc cathode and a catholyte containing from zero to 2 grams of sodium hydroxide per liter. Similarly, the line *HI* represents ratios for making mannitol and a non-crystallizing sorbitol syrup from glucose with an amalgamated lead cathode and a catholyte containing from 10 to 20 grams of sodium hydroxide per liter.

Fig. 9 shows the effect of temperature at 269 and 27 grams of initial sugar per ampere when using amalgamated lead cathodes and a catholyte alkalinity of 10 to 20 grams NaOH per liter. Lines *A* and *B* represent the P.N. and mannitol yield respectively when the ratio is 269 and lines *C* and *D* when it is 27. It will be noticed that line *D* passes through a maximum. This behavior is general. No recoverable amount of mannitol is formed from glucose when reduction conditions are suitable for the production of high purity sorbitol or for syrups which contain practically no sorbitol.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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THE EFFECT OF OXYGEN ON INHIBITION OF CORROSION BY NITRITE[1]

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ABSTRACT

A study has been made of the effects of the concentration of dissolved oxygen and temperature on the rate of breakdown of sodium nitrite in the presence of steel, and on the rate of corrosion of the steel. It was found that, at any given temperature, an increase in concentration of oxygen decreased the amount of nitrite required for inhibition. At high temperatures and low oxygen concentrations it was found that although the rate of corrosion was appreciable the rate of nitrite breakdown was low. In some cases, a considerable time interval before the start of breakdown of nitrite was noted. It was concluded that the mechanism proposed previously for inhibition by nitrite was further substantiated by the evidence presented here.

INTRODUCTION

Corrosion inhibition by sodium nitrite is a problem of both practical and theoretical significance. Corrosion of steel can be prevented in neutral solutions by sodium nitrite. It is of advantage over chromates in that it has no known effect on the skin. Sodium nitrite is of theoretical interest in that it is an inhibiting material which does not form an insoluble salt with iron.

In two previous papers (1, 2) from this laboratory, studies of inhibition by and breakdown of nitrite were reported. The conclusions reached were that the steps leading to inhibition of corrosion were first, the adsorption of nitrite ions at anodic areas, and second, the reduction of this adsorbed nitrite by hydrogen at adjacent cathodic areas to give a protective oxide layer and reduction products of nitrite. This mechanism appears to be a reasonable one from the following considerations:

(*a*) The distances between the oxygen atoms in the nitrite ion and between the iron atoms in a ferrite crystal lattice are very similar.

(*b*) Ammonia may be isolated from the system.

(*c*) Nitrite breaks down only in the presence of corroding steel, that is, when both anodic and cathodic areas are present.

(*d*) Nitrite can accelerate corrosion under some conditions, for example, when the iron is prevented from acquiring a complete oxide layer by the presence of an oxide solubilizer, such as a complex phosphate. In such a case it acts mainly as a cathodic stimulator without being able to complete the oxide layer.

Other experiments reported in the above papers seemed to indicate that the concentration of nitrite required for inhibition depended in part upon the availability of oxygen to the metal surface. It has also been noted by other workers that the relative areas of oxide-covered metal to corroding

[1] Manuscript received July 19, 1948. This paper prepared for delivery before the Chicago Meeting, October 12 to 15, 1949.

metal vary directly with oxygen concentration (3, 4). These two facts seemed to indicate that, at nitrite concentrations just below those required for inhibition, a rise in oxygen concentration would decrease the concentration of nitrite required for inhibition, and that, at lower oxygen concentrations, nitrite might act as a stimulator of corrosion. It was on the basis of these considerations that the present work was undertaken.

EXPERIMENTAL

For this investigation, the constant temperature baths used previously were modified so as to allow gas to be bubbled through the solution. Also, a modified form of the Rocker Immersion apparatus (5) developed here was used.

Methods of analysis

The procedure for determining sodium nitrite was essentially the same as that outlined before. It was found that better sensitivity could be obtained and the time the solution has to be kept at constant temperature

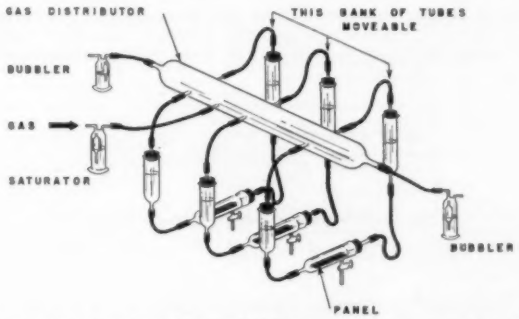

FIG. 1. Perspective drawing of the modified Rocker apparatus showing saturator, gas distributor, and outlet bubblers.

reduced to 30 minutes if the sulfanilic acid was added to the sample before dilution.

The methods used for determining dissolved oxygen were unchanged from those used previously.

Panels

These were again 4 in. x 1 in. (10 cm x 2.5 cm) low carbon, cold-rolled, 24 gauge steel (analysis: C = 0.04, Mn = 0.05, Si = nil, P = 0.008, S = 0.024). The panels used in the constant temperature baths had a $\frac{1}{4}$ in. (0.64 cm) hole drilled near one end; those used in the Rocker Immersion apparatus had none. All panels were first heat-treated at 600 C for one hour and then slowly cooled to room temperature in the oven. Before use the panels were descaled with 6*N* hydrochloric acid containing 2 per cent Rodine,[2] washed in hot water followed by methanol, dried for 10 minutes at

[2] Rodine # 60 was used. It is an aldehyde derivative leaving only a water soluble film, and hence should leave no film on the metal. It is designed specifically for use with muriatic acid by the American Chemical Paint Company.

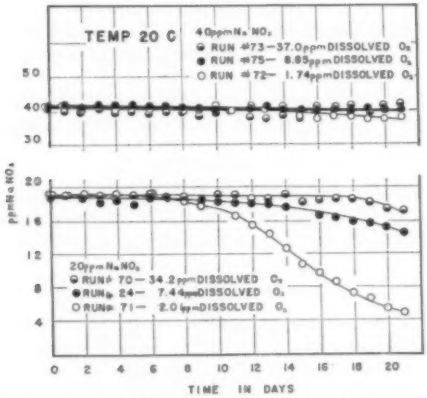

FIG. 2. Effect of oxygen concentration on rate of breakdown of nitrite. The higher concentration of nitrite is more stable, but the decrease in rate of breakdown as the oxygen concentration increases is apparent at both nitrite concentrations.

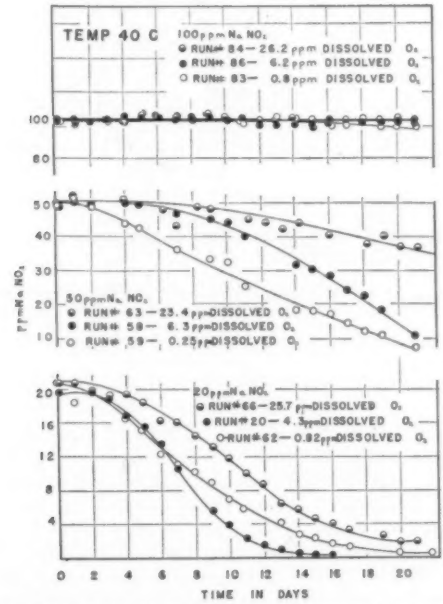
TEMP 40 C
100ppm N_2NO_2
RUN# 84— 26.2 ppm DISSOLVED O_2
RUN# 86— 6.2 ppm DISSOLVED O_2
RUN# 83— 0.8 ppm DISSOLVED O_2
ppm N_2NO_2
50ppm N_2NO_2
RUN# 63— 25.4 ppm DISSOLVED O_2
RUN# 58— 6.3 ppm DISSOLVED O_2
RUN# 59— 0.25 ppm DISSOLVED O_2
20ppm N_2NO_2
RUN# 66— 25.7 ppm DISSOLVED O_2
RUN# 20— 4.3ppm DISSOLVED O_2
RUN# 62— 0.82ppm DISSOLVED O_2
TIME IN DAYS

FIG. 3. Rates of breakdown at 40 C. Note the reversal in rate observed at low nitrite concentrations shown here at 20 ppm. The curves at 50 ppm show a time interval before start of breakdown while there is practically no breakdown at 100 ppm.

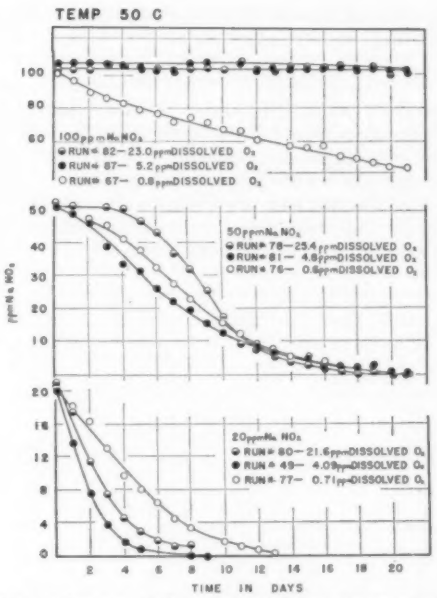
TEMP 50 C
100 ppm Na_2NO_2
RUN # 82— 23.0 ppm DISSOLVED O_2
RUN # 87— 5.2 ppm DISSOLVED O_2
RUN # 67— 0.8 ppm DISSOLVED O_2
50 ppm Na_2NO_2
RUN # 78— 25.4 ppm DISSOLVED O_2
RUN # 81— 4.8 ppm DISSOLVED O_2
RUN # 76— 0.6 ppm DISSOLVED O_2
20 ppm Na_2NO_2
RUN # 80— 21.6 ppm DISSOLVED O_2
RUN # 49— 4.0 ppm DISSOLVED O_2
RUN # 77— 0.7 ppm DISSOLVED O_2
ppm Na_2NO_2
TIME IN DAYS

FIG. 4. Rates of breakdown at 50 C. A reversal in rate is observed again at 20 ppm. At 50 ppm, the effects of small oxide covered areas and the time interval before breakdown are apparent. At 100 ppm oxygen aids nitrite in acting as an inhibitor.

TABLE I. *General data for tests made with sodium nitrite in breakdown baths*

Area of specimen = 0.5 dm^2

Duration of tests = 3 weeks or as on graph

Series No.	Initial $NaNO_2$	Temperature	Oxygen				Air				Nitrogen			
			Dissolved oxygen	Weight loss	pH		Dissolved oxygen	Weight loss	pH		Dissolved oxygen	Weight loss	pH	
					Initial	Final			Initial	Final			Initial	Final
	ppm	C	ppm	grams	25 C	25 C	ppm	grams	25 C	25 C	ppm	grams	25 C	25 C
1	20	20	34.2	0.0098	7.4	8.3	7.4	0.2146	7.4	7.6	2.0	0.4928	7.4	7.5
2		40	25.7	1.8624*	7.4	8.6	4.3	1.2127	7.7	8.0	0.8	0.7270	7.7	8.0
3		50	21.6	2.8531	8.1	8.5	4.1	1.7274	7.6	8.2	0.7	0.5471	8.4	8.8
4	40	20	37.0	0.0012	7.4	7.2	8.8	0.0042	7.6	8.6	1.7	0.0503	7.7	7.6
5	50	40	23.4	0.3907	7.5	8.0	6.3	0.8369	7.3	8.6	0.3	0.7318	6.8	8.7
6		50	25.4	1.0768	7.5	8.0	4.8	1.2601	7.6	8.0	0.6	1.0414	8.4	8.8
7	100	40	25.5	0.0018	7.5	7.2	6.2	0.0024	7.5	7.1	0.9	0.0088	7.5	7.5
8		50	23.0	0.0036	7.5	7.4	5.2	0.0174	7.5	7.3	0.8	0.7197*	7.2	7.9

* Abraded with #1 emery paper after pickling.

50 C, and finally weighed. At the conclusion of a run, the panels were again pickled, washed, dried, and weighed.

Procedure and results

Constant temperature baths.—In order to insure saturation of the solution with gas and to allow time for the baths to come to temperature, they were filled with Ottawa tap water and allowed to heat overnight with the gas bubbling through the water before the panels were placed in position and the nitrite added. As we had previously satisfied ourselves that nitrite breaks down only in the presence of corroding steel, no blank runs were made. Four steel panels were used in each run.

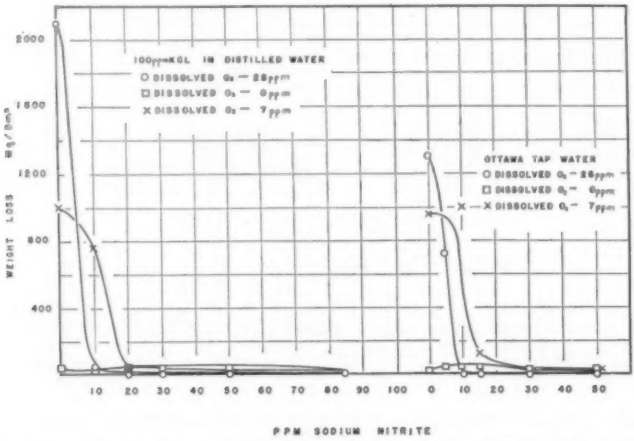
100ppm KCL IN DISTILLED WATER
O DISSOLVED O₂ — 28ppm
□ DISSOLVED O₂ — 6ppm
X DISSOLVED O₂ — 7ppm
OTTAWA TAP WATER
O DISSOLVED O₂ — 28ppm
□ DISSOLVED O₂ — 6ppm
X DISSOLVED O₂ — 7ppm
WEIGHT LOSS mg/dm²
2000
1600
1200
800
400
10 20 30 40 50 60 70 80 90 100 0 10 20 30 40 50
PPM SODIUM NITRITE

FIG. 5. This shows the variation of weight loss with concentration of sodium nitrite and concentration of oxygen as determined with the Rocker Immersion apparatus. There are two sets of graphs, one being for Ottawa tap water at 32 C and the other being for 100 ppm KCl in distilled water at 32 C. The curves are very similar and they both show the tendency of nitrite to stimulate corrosion when both the nitrite and oxygen concentrations are low.

Before the immersion of the panels or the addition of the nitrite, duplicate samples for the determination of dissolved oxygen were removed. At the conclusion of the runs, another set of duplicate dissolved oxygen determinations was made. These values were averaged to give a mean value of the dissolved oxygen content of the solution during the test. Approximately 10 minutes after the immersion of the panels and the addition of the nitrite, two samples were withdrawn, one for a nitrite determination and the other for a pH reading. The nitrite determinations were repeated daily at the same hour and the pH readings were taken weekly. As previously, the duration of the runs was three weeks.

The results of these runs are shown graphically in Fig. 2, 3, and 4, where the concentration of sodium nitrite is plotted against the time in days. Weight losses and pH's obtained during these runs are given in Table I.

An example of a pitted panel obtained at a concentration slightly below that required for inhibition is shown in Fig. 6.

Modified Rocker Immersion.—A perspective drawing of the modified Rocker apparatus is shown in Fig. 1. The solutions were first saturated with the gas to be used by bubbling, and then put in the tubes while the gas was being passed through the manifold. Samples were taken at the beginning and the conclusion of each run for dissolved oxygen concentration and pH measurements. The gases used thus far have been air, oxygen, and nitrogen, as obtained from cylinders and saturated with water vapor by being passed through a bubbler. The pressure in the system was slightly above atmospheric. As with the original apparatus, motion and saturation of the liquid with gas is obtained by an up and down movement of one bank of tubes.

The results of a series of weight loss measurements made with the modified Rocker Immersion apparatus are shown in Fig. 5. Examples of initial and final nitrite concentrations and the pH's for these runs are shown in Table II.

TABLE II. *Illustrative examples of Rocker runs*

Initial nitrite concentration	Final nitrite concentration	Solution	O_2 Concentration	Weight loss mg/dm²	pH
0	0	100 ppm KCl	28 ppm	2100	6.9
20	18	100 ppm KCl	28 ppm	41	6.9
50	47.5	100 ppm KCl	28 ppm	1.6	6.9
100	100	100 ppm KCl	28 ppm	2.0	6.9
0	0	O.T.W.*	0	23	7.3
10	4.3	O.T.W.	0	47	7.6
30	26	O.T.W.	0	34	7.6
100	42	O.T.W.	0	35	7.6

* Ottawa tap water.

DISCUSSION

In all the experiments, the nitrite concentration required for inhibition at any temperature decreased as the oxygen concentration increased. This is true even though the uninhibited corrosion becomes greater as the oxygen concentration is increased.

However, a further examination of the data brings out three main points:

(*a*) In four of the eight series of runs shown in Table I (No. 1, 4, 7, and 8), the relative orders of nitrite breakdown and corrosion rates are the same, that is, the rate of nitrite breakdown increases with increasing corrosion. This was also true for the runs made in air and oxygen with the Rocker.

(*b*) In the other series of runs shown in Table I (No. 2, 3, 5, and 6), the relative orders of nitrite breakdown and corrosion rates are either partly or completely reversed. In these cases, increased corrosion rate due to increased oxygen concentration did not lead to increased consumption of nitrite. In some cases, such as the 50 C runs at nearly zero oxygen concentration, increasing weight losses accompanied increasing nitrite concentrations. This tendency of nitrite to stimulate corrosion at low oxygen concentrations is also shown in the Rocker runs.

(c) In some cases, a time lag was noted before the nitrite began to break down. This time lag was most pronounced at concentrations of nitrite and oxygen which were close to the inhibiting range.

These facts can be correlated in the following manner: When a steel panel is exposed to air it builds up an oxide film. If this panel is then immersed in water containing oxygen there is a tendency for an equilibrium to be established between the areas covered by oxide and the bare corroding areas. The ratios of these areas at equilibrium depends upon the oxygen concentration, the temperature, and the electrolyte content of the solution. Oxygen is acting both to depolarize or increase corrosion and to build up

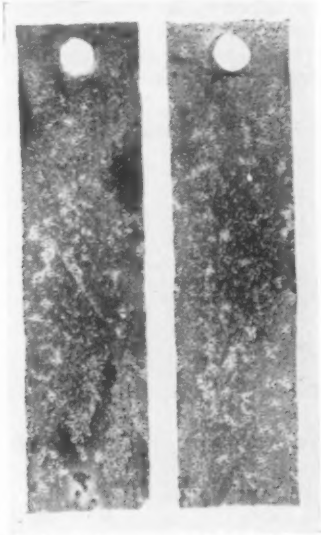

FIG. 6. These panels illustrate the type of bad pitting which can be obtained in sodium nitrite under suitable conditions. They are steel and were exposed in the baths used for breakdown tests to 100 ppm sodium nitrite, 0.77 ppm oxygen at 50 C. Panels exposed to 100 ppm sodium nitrite in aerated solution at 50 C showed no evidence of corrosion whatsoever.

oxide film. If sodium nitrite is present in the solution also, any tendency of the oxide areas to decrease is opposed by the nitrite which tends to extend the film. If the areas covered by oxide are relatively large and sodium nitrite is present in sufficient amount to complete and repair the oxide film either wholly or almost wholly, inhibition or near-inhibition is attained. In such a case, the rates of nitrite breakdown and corrosion will follow the same pattern. This would account for the first set of observations.

When the conditions in the solution are such that the oxide-covered area at equilibrium is small and the nitrite is present in insufficient quantity to extend the film more rapidly than it is being destroyed, the rates of nitrite breakdown and of corrosion do not follow the same pattern. If the oxide

areas are very small then the corrosion will be mainly controlled by oxygen depolarization, but nitrite breakdown will be controlled by the total length of boundary between oxide and bare areas. When this is small, nitrite will stimulate rather than inhibit corrosion. This would account for the second set of observations and is also corroborating evidence for the postulate that nitrite acts to extend the oxide layer by adsorption on the anodic areas followed by reduction by cathodic hydrogen at the junctions of anodic and cathodic areas.

At high concentrations of nitrite, the initial rate of repair of the air-formed film may be sufficient to maintain an unstable film which protects for some time. This film will tend to remain because a complete film will have some stability due to lateral cross-bonding in the oxide. However, once this film begins to break down, if the rate at which nitrite builds up film is less than the rate at which the film itself breaks down, then both corrosion and nitrite breakdown will occur. This film will, of course, last longest in solutions near the inhibiting range.

CONCLUSIONS

1. An increase in oxygen concentration decreases the concentration of sodium nitrite required for inhibition of steel corrosion.
2. On the basis of the mechanism of inhibition by nitrite proposed in an earlier paper, it is possible to explain the results presented here.

Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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SALT-BATH CHROMIZING[1]

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ABSTRACT

A variety of ferrous materials has been satisfactorily chromized at temperatures from 900 to 1200 C by immersion in fused salt baths containing from 5 to 30 weight per cent chromous chloride. The rate of case formation is equal to or greater than that obtained with the various pack methods at corresponding temperatures. The chromous chloride may be prepared in situ by the reduction of chromic chloride with chromium metal.

INTRODUCTION

The resistance of chromium and chromium-containing alloys to corrosion under oxidizing conditions is well known. The maximum temperature for stability in air, for example, increases from about 500 C for iron to about 900 C for chromium and up to 1050–1100 C for a 25–30 per cent chromium steel.

Since only the surface of a corrosion-resistant alloy is effective in opposing destructive attack, there are many instances in which ordinary iron or steels having a protective high-chromium alloy surface are as satisfactory from a performance standpoint as a continuous "stainless steel" structure. Recognition of this fact has led to the development of the various chromizing processes in which a protective case containing from 40 to 70 per cent chromium at the surface is produced by heating the base either in contact with chromium metal or in an atmosphere containing a chromium halide.

The principal method in use at present is the pack process in which a chromium-containing mixture is packed around parts in a tubular furnace, and the charge heated to 1300–1400 C in a hydrogen atmosphere (1). Variations which permit the use of lower temperatures include the use of a H_2-HCl atmosphere with a charge of chromium metal or ferrochromium, and the use of a chromous chloride-impregnated ceramic pack in an inert or reducing atmosphere.

A much more flexible process is the salt-bath method used in experimental work in Germany during the war. In this process, chromizing is obtained by simply immersing the work in fused salt containing chromous chloride (2), (3), (4).

Obvious advantages of this method include such factors as greater latitude in chromous chloride concentration during treatment, elimination of packing and unloading operations and furnace heating and cooling, and the possibility of chromizing, simultaneously, articles requiring different periods of treatment. These advantages prompted a more thorough investigation of the process to determine its feasibility. This investigation was undertaken at Battelle Memorial Institute in 1948 under the sponsorship

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of the Army Air Forces' Air Materiel Command, which was interested in chromized steels as replacements for strategic materials in aircraft. Results of this work are summarized here.

THE CHROMIZING MECHANISM

Salt-bath chromizing, like all of the pack processes except those depending solely on the diffusion of metallic chromium, is a displacement process. In the chromizing of steel, chromous chloride reacts with iron to form a chromium-iron alloy and ferrous chloride (5), (6). To prevent the accumulation of ferrous chloride which would restrict the chromizing reaction, metallic chromium is added to the bath. At the surface of the chromium the reverse reaction occurs, with the reduction of ferrous chloride and the formation of additional chromous chloride. The surface of a chromized part as ordinarily prepared is never pure chromium, but is of the order of 40 to 70 per cent chromium. The concentration gradient beneath the surface drops to about 13 per cent at the interface between the case and base metal.

The rate of case formation in the salt bath is dependent upon two processes: (*a*) the exchange reaction outlined above and (*b*), the interdiffusion of chromium and iron. In salt-bath chromizing with a high chromous-ion activity, the limiting factor is the diffusion process, and the exchange process can, for practical purposes, be assumed to be instantaneous. Since the diffusion rate is an exponential function of the temperature, the rate of case formation increases rapidly with a small temperature increase.

Preparation of reagents

Chromic chloride.—It was first necessary in this investigation to work out a convenient method for the preparation of chromous chloride in quantities required for the salt-bath operations. Although several methods are available, the reduction of anhydrous chromic chloride in a hydrogen-hydrogen chloride atmosphere was selected as the most convenient for laboratory-scale operations.

High-purity anhydrous chromic chloride was prepared by chlorination of electrolytic chromium flake, with tank chlorine in a horizontal silica-tube furnace at temperatures from 700–900 C. The rate of reaction was controlled by regulating the rate of gas flow and the furnace temperature. In the initial stages of the chlorination, the furnace temperature was maintained at 700 C, the higher temperature being used at the end of the run to obtain complete conversion of the metal to the chloride. Since the anhydrous chloride is stable toward moisture and air, no handling precautions were necessary.

Chromous chloride.—Chromous chloride is extremely hygroscopic and it must be prevented from coming into contact with air or moisture if contamination is to be avoided. Although it can be prepared in the bath by reducing chromic chloride with chromium metal, in the exploratory work it was prepared by reducing the chromic chloride at 500 C in a hydrogen atmosphere containing 2 per cent hydrogen chloride by volume (7). By preparing each charge separately in individual ampules, a high-purity product was obtained that could be transferred to the salt bath with a

minimum of contamination. Hydrogen chloride was added to the hydrogen to prevent reduction to the metal in localized areas. When a high-purity product is not required, however, the hydrogen chloride can be eliminated from the reduction treatment since there is, under proper conditions, only limited reduction to metallic chromium in its absence. Completion of the reduction was determined by visual examination of the charge, although control could have been effected by checking the evolution of HCl. To avoid contamination, the chromous chloride was poured directly into the bath under a protective atmosphere.

Production of chromous chloride by reacting chromium metal with dry hydrogen-chloride gas was unsatisfactory because it was difficult to obtain complete conversion. The chromous chloride produced in this way formed a protective barrier on the residual metal, thus retarding further reaction.

Internal reduction of the anhydrous chromic chloride proved very successful. The fused diluent components of the bath were held at 900 C or below for 1 to 3 hours to permit rapid conversion to chromous chloride with a minimum loss of the chromic chloride from volatilization. The bath temperature was then increased to the previously selected chromizing temperature.

Salt-bath chromizing

Essentially, the laboratory salt-bath chromizing furnace consisted of a heated crucible with provisions for manipulation of specimens and maintenance of predetermined temperatures and atmospheres (Fig. 1). A replaceable cylindrical ceramic crucible was placed at the bottom of a closed end vertical stainless-steel tube. The lower part of this tube containing the crucible was located in a globar-heated sheet steel and insulating brick shell. The globar elements were arranged vertically and concentrically around the steel tube. Protection of the lower tube exterior against scaling at chromizing temperatures was obtained by painting the surfaces adjacent to the heating elements with a high-temperature porcelain-type ceramic enamel developed at Battelle Memorial Institute. The tube top projected far enough above the shell so that it remained cool during operation. It was fitted with a large rubber stopper, gas inlet and outlet tubes, and openings for suspension wires.

Several runs were made in an internally heated type P Ajax electric salt-bath furnace. This furnace has a 15-kw, 220-volt, 72-ampere rating. The furnace was equipped with a ceramic pot 10 inches (25.4 cm) in diameter and 15 inches (38.1 cm) in depth. A stainless-steel and brick cover was built over the top to retain an atmosphere over the bath.

The primary salt-bath composition used in a majority of runs consisted of the following mixture:

30% $CrCl_2$
49% $BaCl_2$
21% NaCl
Sufficient Cr flake to cover the crucible bottom.

An argon atmosphere was provided to shield the bath against air. Comparative case formation determinations were made in the above bath and with this atmosphere. However, variations were made on both bath composition and atmosphere to estimate results on chromizing.

The sodium and barium salts were first charged into the crucible and heated to the fusion point under argon atmosphere. Then the chromous salt and chromium metal were introduced, also under atmosphere. After the charge had reached operating temperature, suspended specimens were lowered into the bath, and then pulled out after required treatment times. It was found necessary to cool the specimens in an inert or reducing atmosphere to avoid superficial heat staining of the work. Variations in this basic

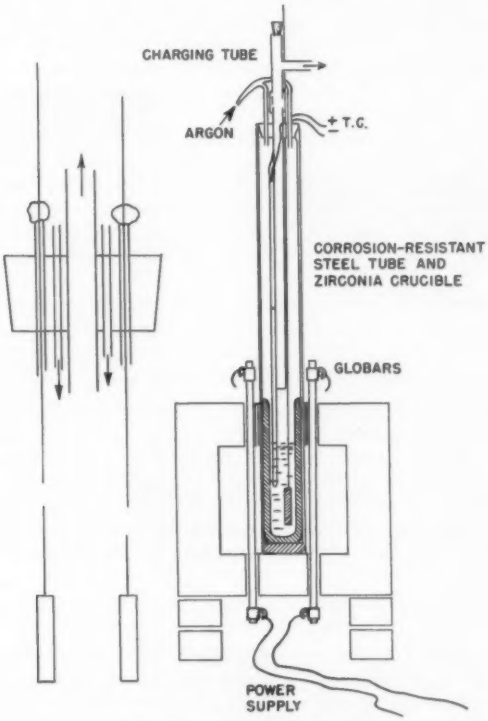

FIG. 1. Chromizing furnace

procedure included variations in salt-bath composition, atmospheres, temperature, time, materials, and minor manipulative details.

Some work on pack chromizing was carried out to provide a basis for comparison with the salt-bath method. A vertical globar-heated steel-tube furnace was employed in this connection. In addition to temperature controls, a hydrogen-anhydrous hydrogen chloride gas system for providing a steady gas flow through the furnace was used. This included a hydrogen purification train for removing traces of oxygen and moisture. Following general procedures for pack chromizing, specimens were lowered into the tube, a mixture of two parts ferrochromium to one part alumina was poured

in around them after which the tube was capped and heated during inflow of the gas mixture.

Examination of specimens

Specimens, after treatment, were first inspected visually as to uniformity, continuity, and appearance of the surface, and then subjected to acid-immersion tests and metallographic examination.

The acid test employed consisted of immersion in a 1:2 concentrated nitric acid, water solution at room temperature. Specimens having continuous cases were unaffected in 3- to 4-month test periods. Those having slight porosity or excessively thin cases failed within a few hours. Information from this test could not, of course, be used as an indication of corrosion resistance under different conditions.

The principal criterion used in evaluating the cases was metallographic examination. This involved transverse sectioning of the piece, mounting in bakelite, polishing, etching, and examination under various magnifications. Case-thickness measurements were made either on a Bausch and Lomb Research Metallograph using a measuring eyepiece, or on a Tukon hardness machine. Thickness, regularity, soundness, and structural details were noted.

In a few instances Knoop hardness, bend, and Magnegage tests were employed.

RESULTS OF EXPERIMENTAL WORK

Successful salt-bath chromizing was carried out on a variety of ferrous materials. Smooth, nonporous, deformable, nitric-acid resistant cases were produced at temperatures between 900 and 1200 C, with chromous chloride concentrations of from 5 to 30 per cent by weight, over one- to six-hour periods. Satisfactory chromizing was also obtained in the Ajax internally heated furnace. The rate of case formation was found to be equal to, or greater than, that obtained with the various pack methods at corresponding temperatures.

The salt bath

The basic salt-bath composition (49% $BaCl_2$, 21% NaCl, 30% $CrCl_2$ plus chromium metal) was found to be quite fluid at operating temperatures. Progressive solidification of this melt apparently began between 500 and 550 C. Penetration into recesses proved to be favorable judging by the uniformity of cases formed. This is illustrated in Fig. 2, showing chromizing in a defect.

The chromous chloride fraction is sensitive to atmospheric oxidation and, therefore, required protection of some kind. Although an enclosed atmosphere top was employed, it is possible that some kind of floating cover might be satisfactory.

In the open air, especially at temperatures above 1000 C, the bath began to lose salt rapidly by evaporation. With enclosed furnaces as used in this work, losses were not significant.

Several initial attempts to chromize in the absence of chromium metal

in the charge were unsuccessful. This was true even of runs in which a single specimen was treated in a virgin bath. Therefore, all succeeding runs were made with this present, as previously mentioned.

Although good cases were formed on iron and steel in the reference bath, some variations were investigated in a search for more economic operation. Calcium fluoride and sodium fluoride were substituted for the more volatile barium and sodium chlorides. The fluoride bath proved to be sufficiently fluid at operating temperatures (900–1200 C), salt vaporization was reduced, and good case structures were formed. A disadvantage appeared to be the difficulty in rinsing adhering salt after chromizing.

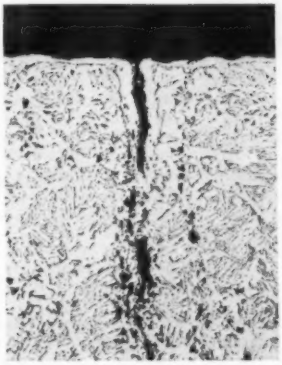

FIG. 2

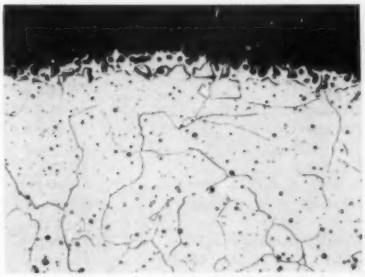

FIG. 3

FIG. 2. S.A.E. 5115 steel, salt-bath chromized at 1100 C (2000F) showing penetration into defect. Nital etch, × 50.

FIG. 3. Irregular porous case on Armco iron, salt-bath chromized at 1100 C (2000 F) under air. Nital etch, × 50.

To determine how much the chromous chloride concentration could be reduced and still permit the production of satisfactory cases, a series of runs were made in which the chromous chloride varied from 50 to 2 per cent by weight. A 5 per cent bath appeared to constitute the practical lower limit, but a 10 to 20 per cent bath yielded more satisfactory results.

Attempts to substitute chromic chloride for the chromous salt failed in repeated trials. In every instance, severe corrosion of the specimens occurred. Favorable results from the use of a chromic chromous mixture as reported by Bennek *et al.* (4) could not be duplicated in this work. In every case, the specimens were badly corroded by the bath.

Nitrogen, carbon dioxide, and air atmospheres were also tried. The first two provided protection without interfering with chromizing. Good cases were obtained in air where bath vapors were sufficiently undisturbed to provide a barrier at the bath surface. Where air currents had free access to the bath surface, severe oxidation and vaporization occurred. Fig. 3 shows a structure typical of those obtained from an oxidizing bath.

Materials chromized

Metals and alloys chromized in the small experimental furnace are listed in Table I. The 49%-21%-30% salt bath was used, and an argon atmosphere was provided. Rates of case formation on Armco iron are shown in Fig. 4. The effect of temperature on the rate of diffusion is evident.

TABLE I. *Effect of treating time on case thickness of various chromized materials*

Material	Shape	Chromizing temperature	Case thickness (mm)			
			Salt-bath method			Pack method
			1 hr	3 hr	6 hr	6 hr
Armco iron	5 mm rod	1200 C	0.109	0.208	0.305	—
Armco iron	5 mm rod	1100 C	0.061	0.112	0.147	—
Armco iron	5 mm rod	1000 C	0.020	0.046	0.058	0.018
Armco iron	5 mm rod	900 C	0.009	0.018	0.025	—
SAE 1015 steel	6.5 mm x 6.5 mm bar	1100 C	0.013	0.028	—	—
SAE 1045 steel	6.5 mm x 6.5 mm bar	1100 C	0.010	0.020	0.030	—
SAE 2315 steel	6.5 mm x 6.5 mm bar	1000 C	0.010	0.020	0.030	0.013
SAE 3140 steel	6.5 mm x 6.5 mm bar	1000 C	0.013	0.025	0.033	0.010
SAE 4120 steel	6.5 mm x 6.5 mm bar	1000 C	0.013	0.015	0.023	0.015
SAE 4130 steel	6.5 mm x 6.5 mm bar	1100 C	0.015	0.020	0.025	—
SAE 5115 steel	6.5 mm x 6.5 mm bar	1100 C	0.010	0.015	0.020	—
2% Mn, 0.15% C, 0.8% Si steel	5 mm rod	1100 C	0.015	0.030	0.048	—
1.5% Mn, 0.08% C, 0.4% Si, 0.64% Ti ("IK" type steel)	6.5 mm x 6.5 mm bar	1100 C	0.035	0.058	—	—
18-8 Type 347 stainless steel	5 mm rod	1200 C	—	—	0.084	—
3.3% C, 1.7% Si, 0.8% Mn, cast iron	8 mm rod	1035 C	—	0.024	—	—
3.4% C, 1.9% Si, 0.08% Mn, cast iron*	8 mm rod	1000 C	0.010	—	0.023	0.015
Nickel	6.5 mm rod	1200 C	0.018	—	0.051	—
Molybdenum	2 mm rod	1200 C	—	—	0.033	—
Tungsten	8 mm rod	1200 C	—	—	0.005	—

* Partially decarburized to depth of 8 mils.

Case structure

The relation of structural details to the Fe-Cr constitution diagram is shown in Fig. 5 and 6. The outer band is alpha, solid solution of chromium in iron. The inner band, separated by a fine line, is transformed gamma phase. The two-phase gamma loop appears as an interface between these bands, in conformance with phase rule considerations. The heavy line represents the limit of chromium penetration. Heavy lines in the outer section of the case are crystal boundaries and not cracks.

Case thicknesses

Case thicknesses on the steels of Table I varied from .015 mm to .03 mm after a three hour treatment. An "IK" type steel, used in German chromizing practice (8), (9), accumulated a .06 mm case under identical conditions. This provides an example of greater penetration by the use of a steel having superior chromizing properties. The penetration rates in the steels investigated did not always vary inversely as their carbon contents, because of

other variables. In general, however, the presence of carbon sharply restricts the rate of case growth as illustrated in Fig. 7 and 8. In German "IK" type steels, it has been the practice to hold the carbon content down and/or to stabilize it with titanium or some other strong carbide former.

In a number of runs, cast iron was found to chromize without difficulty, a uniform corrosion-resistant .025 mm case being formed in three hours at

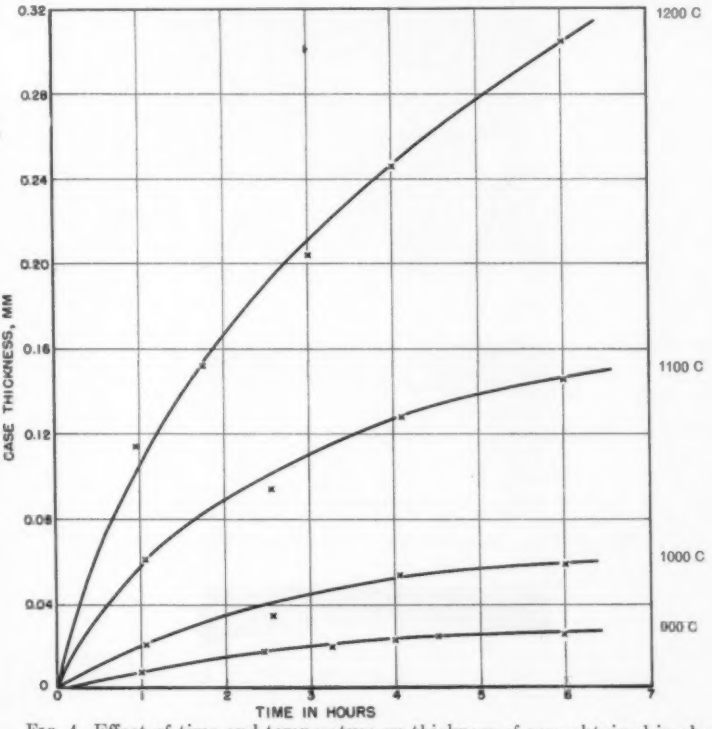

FIG. 4. Effect of time and temperature on thickness of case obtained in chromizing Armco iron by the salt-bath method.

1035 C (Fig. 9). The effect of excessive carbon is partially offset in the case of cast iron by its lower melting point. Decarburization did not increase chromium case thickness. Heavy cases were produced on the stainless steel and nickel of Table I. Molybdenum received only .010 mm after 3 hours at 1200 C, and tungsten only .005 mm at this temperature.

Results of runs made in the Ajax internally heated furnace were similar to those covered by Table I. Barium chloride and sodium chloride were first melted. Sufficient chromic chloride was then added to produce a 20 per cent chromous chloride bath by reduction with chromium metal. After addition of the chromium, the bath was held at 900 C or below for 3 hours

to avoid excessive $CrCl_3$ loss during the reduction period allowed. Following this, the temperature was increased to 1000 C and the specimens were introduced. No operational difficulties were encountered. Results were

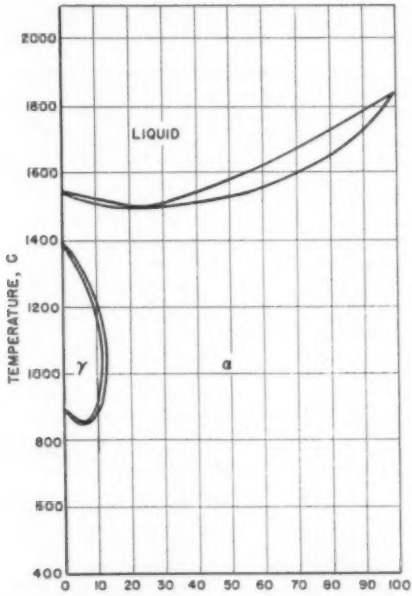

FIG. 5. Iron-chromium temperature-composition diagram

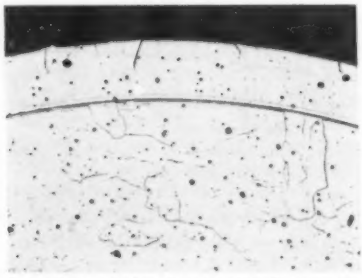

FIG. 6. Armco iron chromized at 1200 C (2200 F). Concentrated HCl etch followed by nital, × 50.

similar to those obtained in the smaller bath. It was necessary to cool specimens in atmosphere on their way out of the furnace to avoid heat stain.

Case hardnesses on iron were found to be fairly soft (170–180 Knoop),

and deformable, confirming previous reports in the literature (10). Although no hardness measurements were made on higher carbon steel cases, these are reported to be considerably harder.

None of the materials listed in Table I failed to pass the nitric acid test after chromizing. Even continuous cases as thin as .005 mm passed tests of several months duration.

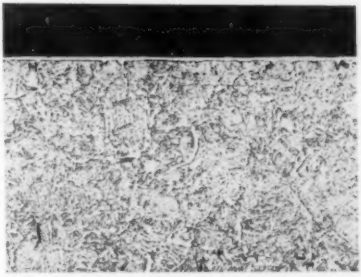

FIG. 7

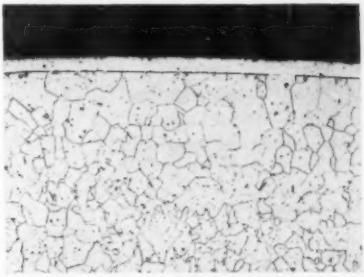

FIG. 8

FIG. 7 and 8. Showing comparative case-formation rates. Upper (Fig. 7) is an S.A.E. 4120 steel, chromized for 2 hours at 1100 C. Lower (Fig. 8) is iron chromized for 2½ hours at 1000 C. Nital etch, × 50.

Comparisons of cases formed in the salt bath with those formed by the pack method are shown in Table I. Allowing for temperature differences in some instances, the salt-bath method compares favorably.

Estimation of the diffusion coefficient

The diffusion constants D for chromium in Armco iron calculated from the equation $\frac{x^2}{4Dt} = K$ (11), where x is case thickness and t is time, are given graphically in Fig. 10. Assuming the same surface concentration as determined by Hicks (12), K is approximately one.

No provision has been made in these calculations for variation in D with concentration. Good agreement among values of D calculated at the

same temperatures for different times shown in Fig. 4 was taken as an indication that the concentration of chromium at the surface is approximately constant.

The calculated values for the diffusion constant at 1100 C and 1200 C were found to be 2.5×10^{-9} and 9.7×10^{-9}, respectively. These values are of the same order as those obtained by Grube (13) (i.e., $D_{1100} = 8$ to 12×10^{-10} and $D_{1200} = 60$ to 170×10^{-10}) and by Bardenheuer and Muller

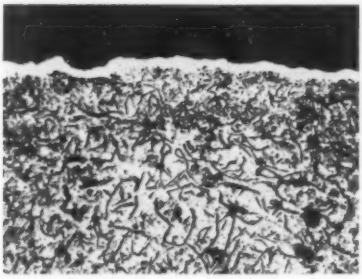

FIG. 9. Cast iron, salt-bath chromized for 3 hours at 1035 C (1900 F). Case thickness: 0.0009 inch (.0029 cm). Picral etch, × 50.

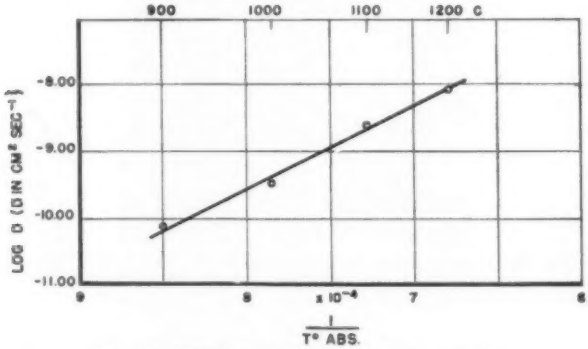

FIG. 10. Diffusion of chromium in Armco iron

(13) (i.e., $D_{1150} = 6.8 \times 10^{-10}$ and $D_{1300} = 5.3 \times 10^{-8}$). The characteristic diffusion curve relating the diffusion constant to the absolute temperature as shown in Fig. 10 is an indication of the precision of the experimental values.

Evaluation of the process

From the standpoint of costs, the salt-bath method compares favorably with other chromizing processes. The bath can be operated in a more or less continuous manner so that packing, furnace heating, furnace cooling,

and unloading cycles are avoided. Although chromium metal was used in producing chromic chloride in this project, this salt can be more cheaply made from ferrochromium (14), (15). Operation at lower temperatures for shorter times is possible and many of the inherent advantages of heat treating salt baths carry over to the chromizing bath. A principal advantage, compared to pack methods, is the greater range of $CrCl_2$ concentration available.

The effectiveness of the fused-salt chromizing is dependent to a considerable extent, as in other chromizing methods, on choice of material. Although protective cases will form on a wide variety of materials, deeper penetration at lower temperatures requires the selection of lower carbon steels (16). Silicon appears to increase the diffusion rate, but specific effects of other elements, alone or in combination, are not well known.

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Any discussion of this paper will appear in the discussion section of Volume 96 of the TRANSACTIONS of the Society.

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